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BACHELOR THESIS

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**Inducing Two-way Shape Memory Effect
in NiTi-polymer Composite**

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Název práce: Vyvolání obousměrné tvarové paměti v NiTi-polymerovém kompozitu

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Abstrakt: Obousměrná tvarová paměť umožňuje deformaci materiálu mezi dvěma zapamatovatelnými tvary bez působení vnějších sil, přičemž aktivaci změny tvaru se využívá nejčastěji změna teploty. Mezi řadou způsobů, jak dosáhnout obousměrné tvarové paměti, byla v této práci využita kombinace kovového materiálu Nitinol a vybraného polymeru s tvarovou pamětí. V kompozitním materiálu z těchto dvou složek bylo dosaženo bistabilní obousměrné tvarové paměti. Bistabilní obousměrná tvarová paměť je unikátní tím, že umožňuje existenci materiálu v obou zapamatovaných stavech při stejné teplotě. Bylo prokázáno, že rozhodujícím faktorem pro dosažení určitého tvaru je předešlý teplotní průběh kompozitního materiálu. Pro zlepšené spojení kovového Nitinolu a polymerního materiálu byl povrch NiTi upraven laserem. Mezi několika studovanými polymery prokázal nejlepší vlastnosti polymer vyrobený ze dvou složek, a to 60 % TPU a 40 % PCL. Optimalizovaný kompozitní materiál s dvousložkovou tvarovou pamětí byl detailně charakterizován.

Klíčová slova: vyvolání obousměrné tvarové paměti, Nitinol, polymer s tvarovou pamětí, kompozit

Title: Inducing Two-way Shape Memory Effect in NiTi-polymer Composite

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Abstract: Two-way shape memory effect (TWSME) allows material to actively deform between two remembered shapes without the application of external force. The most common stimulus is temperature change with several approaches to induce shape memory effect in the material. The approach studied in this thesis utilizes Nitinol and shape memory polymer. By combining these two materials, bistable TWSME was induced in the composite. Bistable TWSME allows the material to be in both of its remembered shapes at a single temperature. The shape of the material depends on the temperature profile by which the target temperature was reached. To create the composite Nitinol foil was shape set and its surface laser lined to increase adhesion with the polymer. Out of the studied polymers, the best properties for the preparation of composite were exhibited by a blend of 60 % TPU and 40 % PCL by weight. The composite was then prepared by hot press and tested.

Keywords: inducing two-way shape memory effect, Nitinol, shape memory polymer, composite

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Introduction

Composites are widely used due to their versatility and can be tailored to a specific task. They are made out of distinct constituents that are combined together to achieve new or enhanced physical and chemical properties compared to its constituents. They can also be combined to generate new responses to stimuli from the surrounding environment such as two-way shape memory effect (TWSME) initiated by changes in temperature. The TWSME allows the material to actively deform between two different shapes as a result of stimulation.

To achieve TWSME Nickel Titanium alloy (NiTi) and polymer are often combined. Nitinol exhibits one-way shape memory effect (OWSME) which allows it to recover deformation upon heating. When combined with polymer that deforms it at lower temperatures, the composite can actively change between two shapes. To achieve one of the remembered shape this often requires the temperature of the composite to be elevated and kept above the ambient temperature. To avoid this, a bistable TWSME can be induced. Bistable TWSME allows the material to have either of its remembered shapes at lower temperatures based on the previous temperature profile.

Much of the prior work on bistable TWSME composites with NiTi has been done with three distinct constituents [1–3]. Nitinol, one polymer providing force to deform NiTi and fixating polymer. This increases the number of interfaces within the composite. Failure of the interface between constituents is called delamination and is the most common failure mode of composites. The present study aims to eliminate one of the interface layers by combining the Nitinol with shape memory polymer. Shape memory polymers have the potential to provide both the fixating and recovery capability of the two separate polymer constituents. In particular, this study aimed to identify shape memory polymers potentially compatible with Nitinol, test their shape memory properties and prepare and test the final composite.

Chapter 1

Theoretical Background

1.1 Composite Materials

Composite materials are a class of materials that are made out of two or more constituents. These materials are combined to produce a final product that exhibits enhanced performance characteristics compared to its individual components. These enhanced properties can be tailored according to the requirements of the application such as higher melting point or superior chemical resistance. Composites can also be tailored to exhibit new behaviour to fulfil a certain task. Because of these advantages composite find a wide variety of application in fields ranging from construction to aerospace and medicine.

Composites can be divided into three main types. Well known are fibre-reinforced composites. They are made by embedding high strength fibres, such as glass or carbon, in a matrix material, often a polymer. These composites include glass fibre composites and their more modern counter parts carbon fibre reinforced composites.

Second are particle composites. In these composites, one of the constituents form a matrix in which the other material is dispersed in a form of distinct particles. Common example of these are ceramics.

Third are structural composites sometimes referred to as sandwich composites or laminates. These composites utilise layers of constituents that are placed on top of each other with an interface layer in between. They are widely used in automotive and aerospace sector in components from tyres to wings.

The common issue of all composites is the strength and longevity of interface

between the constituents. The interface layer is crucial in the performance of composites. It transfers all the load and stresses on the composites and thus allowing the separate constituents to combine their properties and become a single material. This problem is especially profound in structural composites. This is caused by the load having to be carried through several layers to a constituent that has the best properties to resist it.

1.2 Nickel Titanium Alloy

Nickel-Titanium alloys, also known as NiTi or Nitinol, have seen an ever-increasing range of use since the time of their discovery in 1960s. The alloy has many interesting properties such as corrosive resistance, biocompatibility and most importantly shape memory property.

The shape memory property of Nitinol allows the material to return upon heating to its original shape even after it has been seemingly plastically deformed. This makes it possible to be used as an actuator on its own. With right tailoring of micro-structure, NiTi can also achieve super-elasticity. These properties can be utilised in applications with high limitations for weight, complexity and space occupation. As a result, this material is widely used in aerospace and medical industries.

1.2.1 One-way Shape Memory in Nitinol

One-way shape memory effect (further OWSME) in Nitinol is induced by its specific microstructure at different temperatures. The material has two main crystalline structures: an austenitic phase (further referred to as austenite or B2) at higher temperatures with cubic structure and a martensitic phase (further referred to as martensite or B19') at lower temperatures with monoclinic structure. The martensite is either twinned or detwinned which is a key element of Nitinol for the process of shape memory property.

The shape memory effect is achieved through the cycling between the two phases which is illustrated in figure 1.1. The sample is first deformed at martensite through the application of external load. While on the macroscopic scale the deformation appears to be plastic the material has only been detwinned in suitable orientation. Next step is heating the material to be transformed into austenite while the load may or may not be removed. This has the macroscopic effect of the sample returning to its original (parent) shape. Then the sample is once again

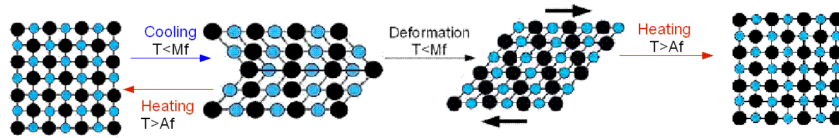


Figure 1.1 One-way shape memory effect in Nitinol [4]

cooled until it is in fully twinned martensite without any external load applied and the process can be repeated again.

The temperatures at which Nitinol transforms from martensite to austenite and from austenite to martensite are not the same. There is a hysteresis that causes the transformation temperatures to differ. Also, the material does not transform after crossing a single temperature value. It is rather spread out across a certain temperature range. This is illustrated in figure 1.2. The marked temperatures have the following meaning:

M_F - Martensite finish temperature, the sample is considered to be fully in martensitic phase

M_S - Martensite start temperature, the sample is considered to have started transforming into martensite

A_F - Austenite finish temperature, the sample is considered to be fully in austenitic phase

A_S - Austenite start temperature, the sample is considered to have started transforming into austenite

The exact conditions under which this process takes place can affect the exact steps in the process. For example, if the applied load is not released after the deformation of martensite then the transformation temperature will be changed. Furthermore it is often the case that a third rhombohedral or R phase is present during the cooling process from austenite to martensite as is visualised in figure 1.3.

1.2.2 Super-Elasticity

Super-elasticity, officially known as pseudo elasticity, is the materials ability to respond elastically to applied load through phase transformation. In Nitinol this is done by tailoring the material to have A_F slightly below the ambient temperature at which the sample operates. Upon load the transformation temperatures shift in the direction of higher temperature. As a result, the sample transforms into martensite and is deforms easily under the applied load. Upon unloading the

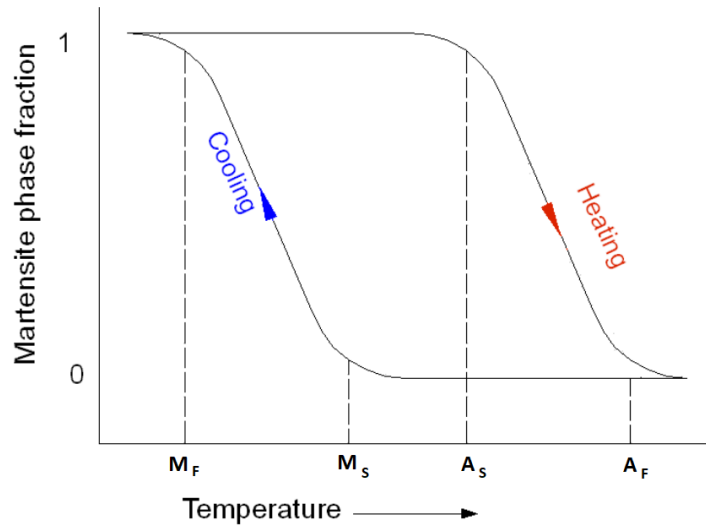


Figure 1.2 Characteristic transformation process of NiTi [4]

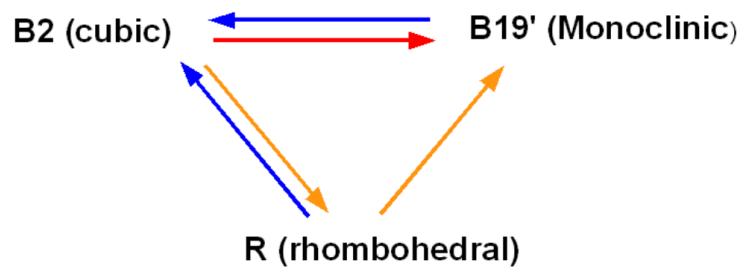


Figure 1.3 Nitinol transformation paths [4]

transformation temperatures once again decrease and the sample transforms back into austenite. On macroscopic scale this appears as if the sample was deformed only elastically.

1.3 Polymers

Polymers are made out of long chains of macro-molecules. They can be either naturally occurring or synthesised. Naturally occurring polymers include DNA, proteins, etc. Examples of synthetic polymers are polystyrene or polyethylene terephthalate (PET). Both synthetic and natural polymers are created by the polymerisation of small molecules known as monomers. Through this and subsequent processes polymers can achieve amorphous or semi-crystalline structures.

Due to their structure, polymers have more than one temperature at which their physical properties change. This is visualised in figure 1.4. At low temperatures polymers behave as a brittle material (denoted as "Glassy Plateau" in figure 1.4) with high Young's modulus. Upon reaching a critical temperature, commonly called glass transition temperature, the material's stiffness decreases sharply until once again it levels out for a wider range of temperatures (denoted as "Rubbery Plateau" in figure 1.4). Within this temperature range the polymer behaves more like a ductile material. This continues until another critical temperature is reached, commonly called melting temperature. Beyond this temperature the polymer behaves as a semi-viscous or viscous material depending on the temperature.

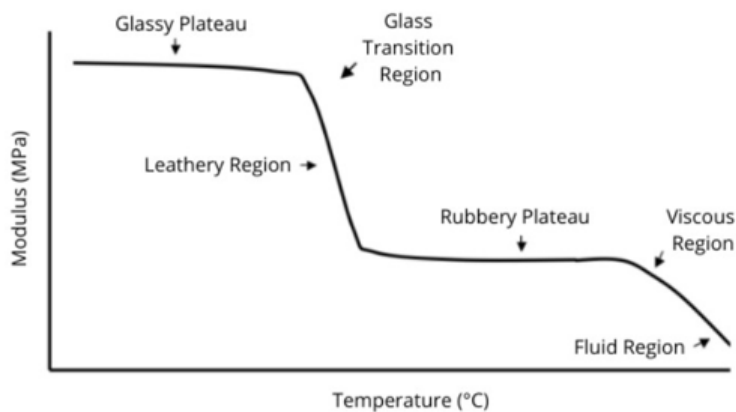


Figure 1.4 Typical relation of Young's modulus and temperature for polymers

Since polymers do not have crystalline structure, it can seem as if they cannot exhibit shape memory property. That is true to the extent that we retain the definition of shape memory as it was for Nitinol. The general relation between the polymer's stiffness and temperature allows for the existence of different type of shape memory [5–9].

1.3.1 One-way Shape Memory in Polymers

The one-way shape memory effect (OWSME) in polymers is based on the existence of net-points in the structure of polymer. These net-points do not degrade until the material reaches melting temperature (T_M). However, large segments of the polymer start to behave as a viscous material upon reaching glass transformation temperature (T_G). The different segments are visualised in figure 1.5a. The critical temperature utilised for OWSME in polymers does not have to be glass transformation temperature and therefore it will be further referred to as the transformation temperature (T_{trans}).

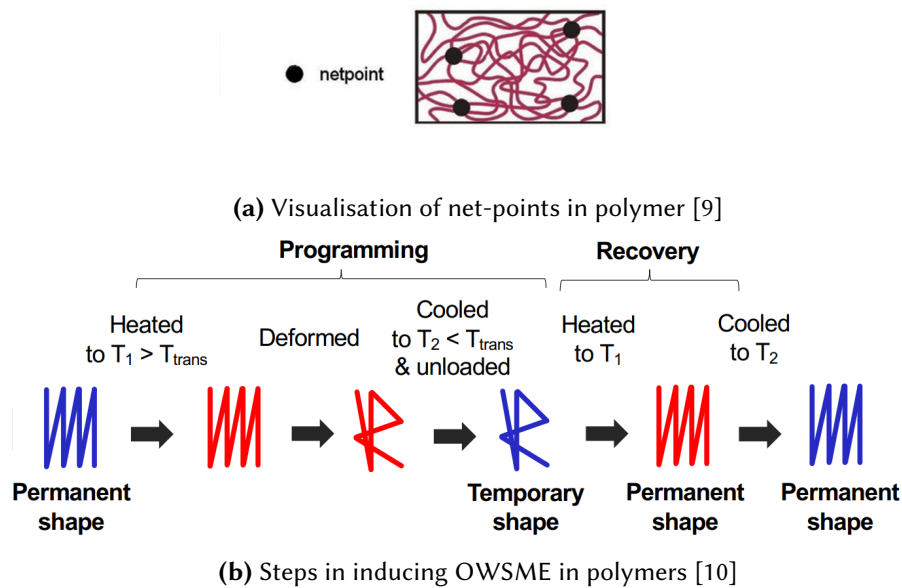


Figure 1.5 One-way shape memory effect in polymers

The process of One-way shape memory can be divided into two segments - programming and recovery as visualised in figure 1.5b. During programming, the material is first heated above the transformation temperature without applying any load. This allows the soft segments of polymer to move. Next, the sample is deformed to the desired temporary shape by the application of load. This is

followed by cooling the sample below the transformation temperature. This forces the previously free moving segments to harden and thus setting the temporary shape. After cooling the load is released from the sample but since the free moving segments hardened in the deformed position, they keep the sample in its temporary shape. Next, the sample is heated above transformation temperature to once again free the deformed segments and the sample returns to its original shape.

There are different ways to create the net-points necessary for this process. The two ways utilised in this work were through crystallisation and through blending of two polymers.

Crystalline Polymers

One way to create net points in polymers is through the crystallisation of the polymer. The development of crystalline structures does not occur in all polymers. It also depends on the process by which the polymer sample is created. The main two factors discussed in this work are the speed of cooling the sample from its melting temperature and subsequent annealing and its parameters.

Polymer Blends

For second type of polymer a blend was considered. Blends are combination of two or more polymers. They can be combined in several different ways such as mechanical mixing, solution blending, melt mixing or reactive blending. The method used in this thesis was melt mixing.

In blends one of the polymers has melting temperature higher than that of the transformation temperature. This means that it takes on the role of net-points in the structure of the blend. The other polymer has a melting temperature equal to T_{trans} . Therefore, it behaves as a viscous material above T_{trans} . Together they create the necessary properties to induce shape memory property in the blend.

Characterisation of Shape Memory Property

Unlike with Nitinol, for polymers it is often the case that they do not recover fully to their original shape. Also, during the removal of load, the sample will recover some of its strain immediately. To evaluate these effects, we introduce two new parameters - shape fixity ratio (R_{fix}) and recovery ratio (R_R). These parameters are defined as:

$$R_{fix} = \frac{\epsilon_F}{\epsilon_D} \times 100\% \quad (1.1)$$

$$R_R = \frac{\epsilon_D - \epsilon_R(N)}{\epsilon_D - \epsilon_R(N - 1)} \times 100\% \quad (1.2)$$

where ϵ_D denotes the strain to which the sample is deformed during programming, ϵ_F denotes strain after cooling below T_{trans} and releasing the deforming load and ϵ_R denotes strain after the recovery phase. The N denotes the number of cycles for which the deformation was measured. This means that the recovery ratio always refers to the shape of sample at the start of that cycle, not to the original shape before testing.

Additional two parameters are used to describe the temperature dependant behaviour of polymer. First, fixation temperature (T_{fix}) is used to describe the temperature at which the polymer fixates its deformed shape. Second, recovery temperature (T_R) denotes the temperature at which the polymer begins to recover its fixated strain.

The fact that polymers can achieve shape memory property has been utilised in a wide variety of fields, such as micro-robotics and medicine. Unlike Nitinol and other shape memory alloys, polymers are significantly cheaper and lighter. They can be also processes into desires shapes using techniques that are not possible or very well developed for metallic alloys. These include ones with high production capacity such as mould injection, or useful for rapid prototyping such as 3D printing. The combination of 3D printing used with materials exhibiting programmable behaviour has been dubbed 4D printing [11].

Furthermore, by utilising different transformation temperatures two-way or multi-way shape memory effect can be achieved in polymers. These critical temperatures can be easily added and tailored by mixing multiple polymers together and changing their mass fraction in the final blend. For further information on shape memory polymer actuators see [10].

1.4 Two-way Shape Memory Effect (TWSME)

While one way shape memory effect (OWSME) requires an external load to achieve its temporary shape, two-way shape memory effect (TWSME) do not require this stimulus. Materials with this property work solely through the thermal cycling the material. The material has two remembered shapes between which it can

transform itself upon either heating or cooling. The specific steps in the two-way shape memory effect can differ. In this thesis two different processes were considered to induce the TWSME in NiTi-polymer composite.

1.4.1 "Constrained" Two-way Shape Memory Effect

One commonly used way to induce shape is by utilising the changing Young's modulus of Nitinol during transformation from martensite to austenite and vice versa [12, 13]. At lower temperatures the polymer deforms Nitinol to desired shape and upon heating the Nitinol transforms into austenite and its Young's modulus increases. As a result, the sample bends in the orientation of the Nitinol parent shape. However, this technique has multiple issues.

First, the polymer is constantly applying load onto the Nitinol and thus the sample cannot fully reach its Nitinol parent shape. This also means that there are constant stresses on acting on the interface layer which is a subject to degradation as a result.

Second, for the composite to be deformed in the parent shape of Nitinol it must be kept at elevated temperature. Unless this is provided by the environment in which composite operates, it must be provided by an additional energy source. While this may not be a problem for some applications it can make this technique of inducing TWSME unfeasible for applications with limited energy sources.

In this work "constrained" TWSME was used mainly to test the adhesion between Nitinol and the net-point creating polymer in blended type shape memory polymer.

1.4.2 Bistable Two-way Shape Memory Effect

In order to solve the problem of "constrained" TWSME a different approach was studied in this thesis. It is targeted at eliminating the need for keeping the composite at elevated temperature to achieve one of its memorised shapes as well as the constant loading of interface layer. To achieve this the composite will utilise the OWSME in polymers as well as in Nitinol. It also introduces new requirement on the polymer. Its transformation temperature (T_{trans}) must lie within the hysteresis window of Nitinol.

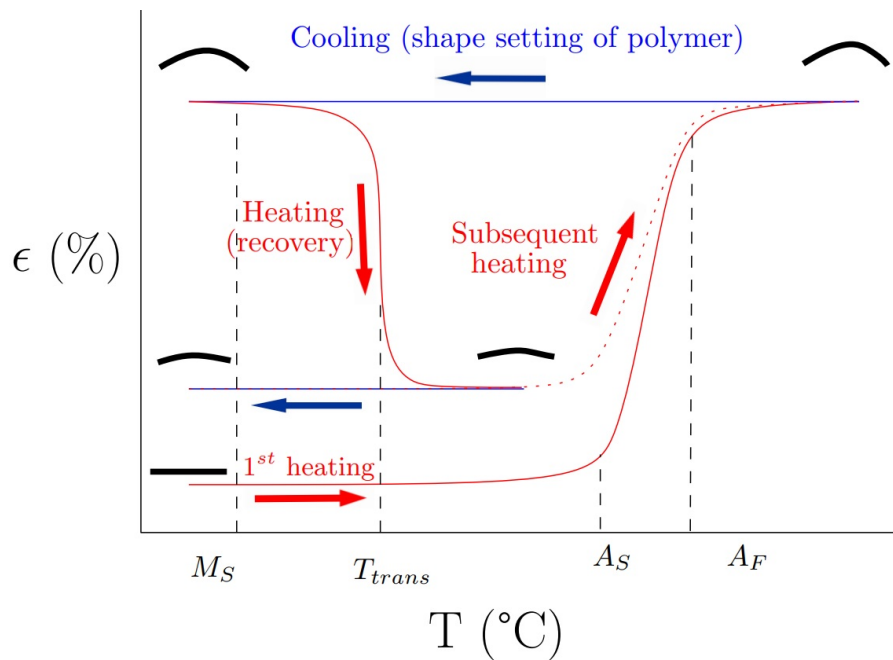


Figure 1.6 Bistable two-way shape memory effect

For illustration of this process let us consider composite with a bent parent shape of Nitinol and a polymer with straight permanent shape. Also, let us start the process below M_S in straight shape as the samples were produced in that shape. The process is also illustrated in figure 1.6.

First, the sample is heated above both the T_{trans} of the polymer as well as the A_F of the Nitinol. This results in the polymer softening. It also means that the Nitinol will deform to its parent shape.

Second, the sample is cooled below the T_{trans} and significantly below M_F . During this process the polymer will fixate its deformation upon being cooled below T_{trans} . Since the M_S of Nitinol lies below T_{trans} the polymer will be fixated in the orientation of the parent shape of Nitinol. The Nitinol will then transform into twinned martensite phase upon cooling below M_S without any change in shape.

Third step requires more delicate temperature control compared to the other steps. The sample is heated above T_{trans} of the polymer but below A_S . This results in the shape memory polymer recovering its original shape. Nitinol will remain in martensite and will be detwinned and thus generate little opposing force to the recovering polymer.

During fourth and last step, the shape of the sample will not change. The sample is cooled below M_S to return to its original state at the beginning of the cycle.

This approach to inducing TWSME successfully tackles the problems mentioned in the description of the latter approach. The deformation to parent shape of one constituent is always accompanied by the reduction of stiffness of the other one. This reduces the problem of the constituents constraining themselves in deforming the composite. This also reduces the stress that is applied on the interface in magnitude and time. Furthermore, it is no longer necessary to continually heat the sample in order to achieve one of the remembered shapes. The process can be interrupted between steps two and three for any amount of time and thus keeping the sample in a different shape than the one at the beginning of the cycle [1–3].

Chapter 2

Aim

The aim of this thesis was to prepare bistable TWSME structural composite. The constituents chosen for this purpose were Nitinol and shape memory polymer.

The first step will be to determine treatment for Nitinol to prepare it for use in composite. The material is often available in the form of straight wires or flat foils. Therefore, a new parent shape will have to be imprinted into the material. This is usually done by annealing the sample at elevated temperature while it is constrained in the desired shape [14].

Also, Nitinol has generally poor adhesion to other materials. For this reason, the surface of the material will have to be altered to increase the strength of the adhesion. The aim will be creating mechanical interlocking patterns into the material. Both processing procedures described above will have to be done without severely diminishing the OWSME of Nitinol.

Second, a shape memory polymer with T_{trans} within the hysteresis window of Nitinol must be identified. To this end several polymers will be chosen and tested for their shape memory properties. This will involve research into the transformation temperatures of different polymers and current literature on shape memory polymers, development of repeatable process for the preparation of samples and their subsequent testing.

Finally, the composite created from the processed Nitinol and selected polymer will be created. This will require the development of process for the preparation of composite with good bonding strength and repeatability. The sample will be then tested for its bistable TWSME.

Chapter 3

Sample Preparation and Processing Techniques

3.1 Preparation of Nitinol

The Nitinol bulk material available for this thesis was in the form of foils with thickness of 100 μm and etched surface from SAES Getters S.p.A.. The chemical composition of the foil was 50 % Nickel and 50 % Titanium by weight. Two types of foil were obtained. One foil exhibited shape memory properties (further referred to as SM foil) and other exhibited super-elastic behavior (further referred to as SE foil). To create smaller strips for further research the foil was cut with scissors. For use in composite the foil had to be further processed to set its desired shape of austenite phase and increase adhesion strength.

Laser Lining of Nitinol

To increase the strength of adhesion between the polymer and Nitinol different surface preparation techniques of Nitinol were considered. Due to low thickness of the foil grinding was discarded as it would be difficult to control the depth of roughening and it would also remove substantial proportion of material's thickness. Therefore, lines were created with laser using laser machine Rod 20 from Narran Ltd. For the process of creating laser lines the samples were super-glued to a plate of stainless steel. This was to prevent the samples from bending during the process and moving the sample's surface out of the focus plane of the laser.

The creation of laser lines, compared to grinding or other surface preparation techniques, has the added benefit of being able to tailor the pattern of lines to

achieve better adhesion. Unfortunately, due to time constraints, the effect of particular patterns was not studied in this thesis. Simple straight lines with set spacing were used [15].

Annealing (Shape Setting) of Nitinol

To set a deformed shape of NiTi the samples were annealed at 400 °C for set amount of time while they were constrained to a certain radius of curvature. This process is called shape setting and works by allowing the deformations in the material to become stable. It is commonly used in training NiTi samples in order to achieve TWSME [14]. This process is often accompanied by changing the transformation temperatures of the annealed sample.

3.2 Preparation of Polymers

Polymer long name	abbreviation	process of inducing OWSME
Poly L-lactic acid	PLLA	Crystallised to generate net-points
Heat deflection polylactic acid	HD PLA	
PA6 + PA6.6	CoPa	
thermoplastic polyurethane	TPU	blended with PCL
poly(ϵ -caprolactone)	PCL	blended with TPU

Table 3.1 Studied polymers

The polymers were obtained in the form of 3D printing filament and had to be formed into different shapes for testing of shape memory property and preparation of composite. Prior to any processing the filament was dried using FilaDryer S2 from Sunlu. Drying settings were different for each filament and the parameters are specified in table 3.2. Afterwards the filaments were kept at room temperature in a closed container with silica-gel to reduce humidity.

The polymer used for "constrained" composite (composite utilizing "constrained" TWSME) was thermoplastic polyurethane (TPU).

Polymers considered for bistable composite (composite utilizing bistable TWSME) were poly L-lactic acid (PLLA), heat deflection polylactic acid (HD PLA), blend of Polyamide 6 and Polyamide 6.6 (CoPa - name specific to bought material) and blend of TPU and poly(ϵ -caprolactone) homopolymer (PCL).

Name of polymer	Drying		Annealing	
	Time (hours)	Temperature (°C)	Time (minutes)	Temperature (°C)
PLLA	6	60	30	100
HD PLA	6	60	20	80
CoPa	10	70	180	90
TPU	10	50	Not annealed	

Table 3.2 Drying and annealing settings for different polymers

Name of polymer	3D printing			Hot press temperature (°C)
	Nozzle (°C)	Bed (°C)	Layer height (mm)	
PLLA	210	60	0.25	-
HD PLA	210	60	0.25	210
CoPa	260	50	0.25	240
TPU&PCL	Not 3D printed			230

Table 3.3 3D printing settings and hot press melting temperature for sample preparation

PLLA was purchased from 3D4Makers B.V, HD PLA from Filamentia (colour graphite), CoPa from Polymaker, PCL from 3D4Makers B.V.,TPU from Polymaker (company assigned name Polyflex TPU90). Their drying settings can be found in table 3.2. PCL was not dried because of its low melting temperature. The filaments were kept in enclosed containers with silica-gel to reduce humidity.

For "crystalline" polymers, samples were first created with FDM 3D printing. However, fast cooling that happens during the 3D printing process does not allow the formation of crystalline structures to occur. Therefore the samples were then annealed to allow for the formation of the crystalline structures (see table 3.2 for specific settings). 3D printing was only used to assess the polymer for the existence of shape memory property as 3D printed parts were not of acceptable quality. They were not uniformly thick, contained voids filled with air and were non-uniformly pre-stressed.

For these reasons, the samples used to determine quantitative values were made through melting of 3D filament and then pressing it in a form to obtain dog-bone shaped samples. For this purpose, YLJ-HP100 from MTI Corporation (further referred to as "hot press") was used. Each of the two dies in YLJ-HP100

can be set separately to a certain temperature in the range from 15 °C (bounded by the coolant) up to 450 °C. The same temperature setting was used for both plates and can be seen in table 3.3. This process allowed for slower cooling of the polymer and thus allowed it to develop crystalline structures. Nevertheless, samples of CoPa were subsequently annealed as they require long annealing time as can be seen in table 3.2. The temperature profile can be seen in figure 3.1. PLLA was discarded during the initial testing and its pressed samples were therefore not made. For HD PLA the samples were not annealed as they were allowed to cool down in the hot press which allowed more than 20 minutes of time between the melting and annealing temperature (cooling process of hot press can be seen in the figure 3.1). The final cross section dimensions of the narrow section of the pressed samples were 3 mm x 1 mm with a length of 13 mm.

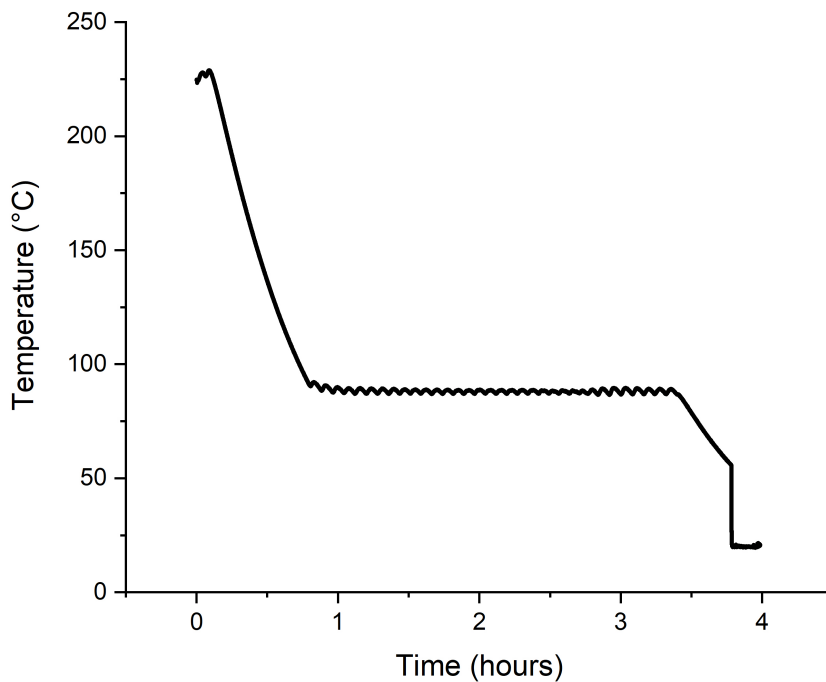


Figure 3.1 Temperature profile used to create the pressed samples of CoPa

For blended polymers, the samples were first melted on a glass plate and mixed using a glass stick. To achieve desired thickness the samples were melted and then pressed. The thickness of the pressed sample was controlled using sheets from stainless steel of known thickness. Afterwards the samples were cut into

dog-bone shape. The resulting cross section of narrow section was approximately 3 mm x 1.5 mm with fluctuation in thickness from 1.3 mm to 1.6 mm. The length of the narrow section was approximately 15 mm.

3.2.1 Notes on the Production Process of Polymer Samples

The production process of samples using hot press went through several iterations prior to achieving a satisfying technique of preparation. The process was initially developed for crystalline samples and then it was altered for preparation of blended samples.

In the first iteration, the polymer was melted on a stainless-steel plate and then it was pressed. The thickness was controlled using sheets of stainless steel with known thickness. The samples would then be cut into dog-bone shape using exacto knife.

An issue arose as an attempt was made to separate the two plates between which the sample was pressed. The sample did not separate from the stainless-steel plate after cooling and the plate was too thick to be easily bent. The samples were successfully removed from the plates without damage when a knife was passed between them and the plate. They did not have a uniform thickness as the melted polymer simply continued to spread after the sample was pressed to desired thickness. Also, it was found that the resulting sample was very difficult to cut even in areas with low thickness. Attempt to cut the sample into dog-bone shape using scissor was unsuccessful as well.

The second iteration was aimed at correcting the issues described above. Approximately 6mm thick slice of 6082 aluminium round timber with diameter of 80mm was cut. Then dog-bone shape cuts were created using cutter and the model of resulting pressing die can be seen in figure 3.2. To achieve easy access to the bottom part of the sample a metal separator denoted with a red colour in the model was used. To separate from the upper plate the pressing die would be covered with baking paper from which the polymer could be easily removed upon cooling.

This approach worked well with HD PLA. For CoPa the separation from the form was not as easily achieved and several samples broke during removal. For blend of TPU and PCL it was not possible to remove the sample. Also, due to aluminium's low hardness the pressing die developed scratches with each removal which caused further complication during the next removal. For this reason, a third and final approach for crystalline polymers was devised.

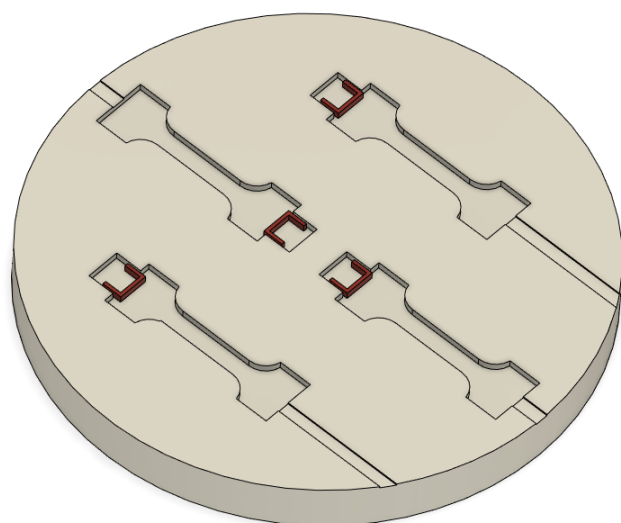


Figure 3.2 Second iteration of approach to polymer sample preparation - pressing die

In third approach the form was created out of 1 mm thick aluminium sheet. To prepare a sample aluminium form was placed on the stainless-steel plate with baking paper in between. Then the 3D printing filament was cut into it. This setup can be seen in figure 3.3a. Next the setup was placed in a hot press and the polymer allowed to melt. Then a second baking paper was placed on top of the sample the sample was pressed. The result can be seen in figure 3.3b.



(a) Setup prior to melting and pressing

(b) Pressed dog-bone sample of CoPa - "fast" pressed

Figure 3.3 Preparation of CoPa sample

This approach worked well for crystalline polymers in terms of creating a repeatable shape and safe removal from the form. The samples can develop voids

and bubbles (see figure 3.3b). This is discussed in detail below. However, for blended polymer this technique did not work, and it could not be removed without damaging the sample. Instead, the sample was melted in a square of toothpicks. These would prevent the polymer to flow easily after it was pressed and thus allowing a bulk amount of the polymer to keep desired thickness. Afterwards the contaminated parts of sample were discarded and from the bulk of the sample an approximately dog-bone shaped sample was cut using exacto knife (example sample is shown in section *Characterisation of polymers* in figure 5.10).

After the development of preparation steps described above several observations were made. The process was sensitive not sensitive to temperature once sufficiently above melting point. However, it was sensitive to the speed at which the sample was pressed and the placing of upper baking paper. Unfortunately, the hot press had a manual wheel that lowered the upper die onto the sample prior to applying load manually by pushing on a lever. Therefore, an attempt to define two speeds was made, further referred to as "fast" and "slow".

"Fast" would be described by the wheel being spun as fast as possible and as a result achieving about 3 rotations per second. This would transfer to speed of about 1.2 cm per second. During pressing that is further referred as "slow" the wheel was rotated approximately once every 30 seconds. Resulting in pressing speed of about 0.07 cm per second.

The problem of placing baking paper on top of the melted sample was the following. If bubbles were trapped between the baking paper and top of the sample, then they would be pressed in and captured by the body of the sample during the pressing and cooling process. The baking paper was therefore placed at one spot in the middle of length of the sample and then spread outwards using a carton. Carton was used to prevent shock cooling the polymer.

The effect of "fast" and "slow" pressing are shown in figure 3.4 where samples produced with different techniques are compared. Difference between placing room temperature stainless steel plate on top of the upper baking paper and directly pressing die onto upper baking paper were tested. The aim was to see whether the shock cooling had effect on the result, but no significant effect was seen.

When the effect of speed of pressing was tested on crystalline polymers only Copo was still considered for the creation of composite.

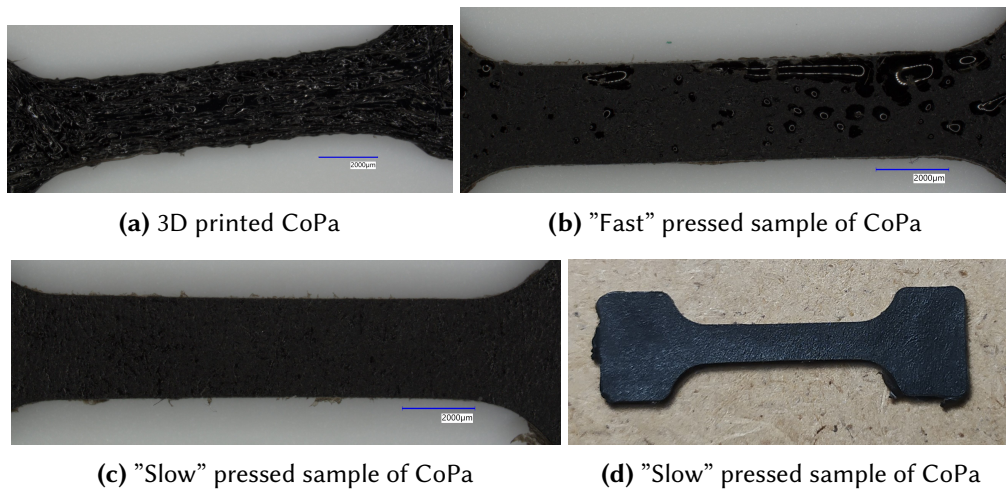


Figure 3.4 Dog-bone shaped samples of CoPa prepared in different ways

For TPU&PCL blend similar results were found. Moreover, a dependence on the thickness of the melted material also affected the quality of final sample. In figures 3.5a and 3.5b the difference between pressing from large bulk of a material and from thickness relatively close to the targeted thickness (referred to as thin) can be seen. It was also discovered that if TPU or TPU&PCL blend was pressed prior to melting, large voids and bubbles would be created in the sample. This is shown in figure 3.5c.

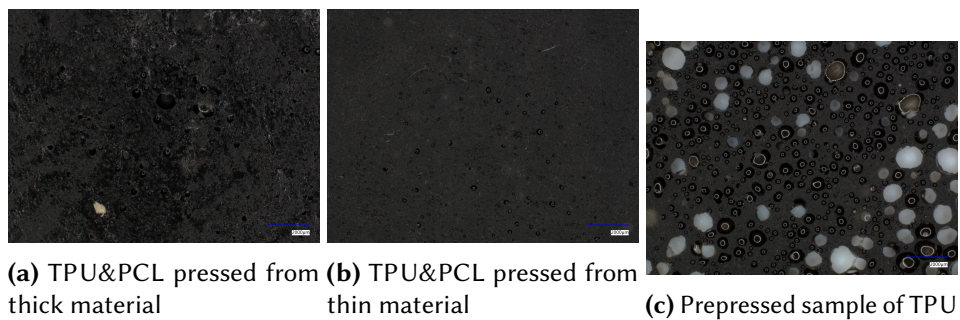


Figure 3.5 Effect of sample preparation on the resulting quality

3.3 Preparation of Composite

To prepare the composite the polymer was melted on both sides of the NiTi stripe and pressed. The aim of this was to negate the effect of different coefficients of thermal expansion for Nitinol ($\alpha_{NiTi} \approx 7 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$) and both TPU and PCL ($\alpha_{TPU} \approx 1.7 \cdot 10^{-4} \text{ }^\circ\text{C}^{-1}$, $\alpha_{PCL} \approx 1.5 \cdot 10^{-4} \text{ }^\circ\text{C}^{-1}$). The total thickness of sample created this way was controlled using sheets from stainless steel of known thickness. After pressing the excess polymer was cut from the sample to achieve a stripe of the same width as that of the NiTi constituent.

3.3.1 Notes on the Preparation of Composite

Similarly, as with the preparation of polymers, the preparation of samples went through two iterations. During the development of the process, it was known that only TPU&PCL blend was a viable option for the preparation of the composite given the shape memory alloy and therefore only it is considered here. This is shown below in section *Characterisation of polymers*.

In first iteration, the Nitinol stripe was placed between layers of polymer and the uncovered ends of the Nitinol stripe were secured from sides with stainless steel plates. This setup can be seen in figure 3.6a. The aim of the plates was to control the thickness of polymer both on top and bottom of the stripe. The targeted thickness of polymer of either side was 1.7 mm. The setup was subsequently placed in the hot press, baking paper placed on top for separation and the polymer was allowed to melt. It was expected that the Nitinol stripe would transform into austenite and bend. This would lift the stainless-steel plates and destroy the setup. Therefore, the upper die of the hot press was lowered just above the stainless-steel plates to prevent them from being pushed away by the Nitinol stripe.

The resulting sample can be seen in figures 3.6b and 3.6c. The first issue that can be seen are the large void that develop on both sides of the sample. Since the Nitinol stripe was secured with plates and the upper die it started to push on the polymer below and above it. This was identified as the main cause of the created voids. Second was the nonuniform thickness of the polymer on top and bottom. It appears that during pressing, the load did not transport well to the bottom side of the sample. As a result, mostly the upper polymer was removed to achieve the controlled total thickness.

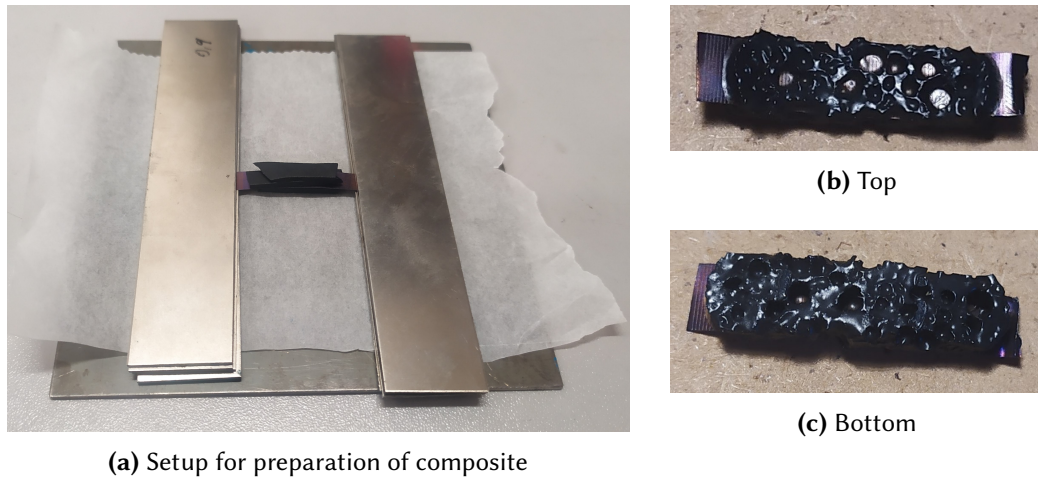
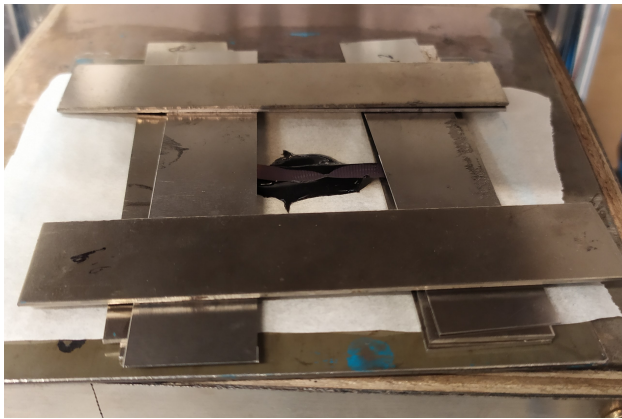


Figure 3.6 First iteration of the preparation of composite (left) and the resulting composite after testing (right)

Second iteration was aimed at correcting the issues described above. In this approach the bottom polymer was melted prior to placing Nitinol stripe on top of it. Also the stainless steel plates were positioned so that the Nitinol would not be able to lift them when it transformed to austenite (this phase of the process can be seen in figure 3.7a). After that the polymer that would create the upper layer of the composite was placed on top of the Nitinol. Following the melting of the upper layer of polymer baking paper was placed on top and the sample was pressed to desired thickness. The resulting sample can be seen in figures 3.7b and 3.7c.

Resulting composite shows severe reduction in voids on the bottom side of the composite. The upper side still has significant number of voids. This has been attributed to the cooling of upper polymer when the upper die is lifted to allow access for placement of upper baking paper. This can be countered by minimising the time the die is elevated and to give time to the polymer to melt between placing the upper baking paper and pressing the sample to desired thickness. The sample also has polymer thickness ratio closer to 1:1 than with the first iteration of the process.



(a) Setup for preparation of composite



(b) Top



(c) Bottom

Figure 3.7 Second iteration of the preparation of composite (left) and the resulting composite (right)

Chapter 4

Methods of Characterisation

4.1 Differential Scanning Calorimetry - DSC

DSC is characterisation technique designed to detect changes of material properties via the change in specific heat capacity. This is done by measuring the temperature of reference sample, measured sample and heat sink. The different amount of heat to samples is proportional to the difference of temperature between both holders. Thus, after the machine is calibrated with a known sample, a quantitative measurement is achievable. This can be used to measure transformation temperatures, heat capacity etc.

In the case of this work DSC was used to determine transformation temperatures of Nitinol (before and after treatments) and polymers. The program used for this purpose was simple temperature cycling between two temperatures (heating/cooling rate of 5 °C per minute) with set time (1 minute) of constant temperature in between. The machine used for these tests was Discovery DSC 25 from TA Instruments. The heating was provided by heating elements and for cooling liquid nitrogen was supplied from external tank.

4.2 Dynamical Mechanical Analysis - DMA

DMA is characterisation technique in which the sample's strain or stress is monitored under different conditions. These conditions can be stress, strain or temperature. The amplitude of stress can be programmed to oscillate to determine the properties of viscoelastic materials: Storage modulus E' (representing elastic component) and Loss modulus E'' (representing viscous component). These properties can be measured as a function of frequency of oscillation, temperature or applied load (stress). The stress may be applied in form of compression, tension,

flexure or shear.

In the case of this work testing in tension was utilised. The machine used for this purpose was Discovery DMA 850 from TA Instruments. The temperature of the sample chamber was controlled via combined effect of heating elements and liquid nitrogen which is supplied from an external tank.

The test profiles used were designed to test the one-way shape memory effect of polymers stress-free (#1) or with applied stress (#2) upon recovery.

DMA Profile #1

Steps of the testing procedure:

1. Heat above T_{trans} at set rate to deformation temperature (T_D)
2. Deform to set deformation strain ϵ_D at set strain ramp rate
3. Decrease temperature below T_{trans} at set rate
4. Release the load
5. Increase temperature above T_{trans} at set rate to recovery temperature ($T_{R,DMA}$)
6. Go back to step 1 for a set number of times

This procedure is designed to evaluate the shape memory property of the polymer. Upon reaching the $T_{R,DMA}$ during recovery the sample was held at this temperature for 10 minutes.

The temperature heating or cooling rate was kept at 5 °C per minute for all tests. The strain rate was 5 % per minute during shape memory evaluation in section *Evaluation of Shape Memory Properties*. In section *Testing the Existence of OWSME in Polymers* the strain rate was actively changed as the value of ϵ_D differed between the runs.

DMA Profile #2

Same as Profile #1 but with additional step after step number 4: Increase the stress to set value at a set stress ramp rate. This testing profile was designed to evaluate the evolution of OWSME in polymer over cycles with load applied upon recovery.

A third testing profile was envisioned. The difference between it and the *DMA profile #2* would be that instead of increasing stress upon releasing the load, it would fix the strain of that sample. This way the force that the sample could generate upon recovery would be measured. Unfortunately, DMA 850 did not have an option of fixing an inherited strain. The system could only fix preset strain.

4.3 Thermomechanical Analysis - TMA

TMA is a characterisation technique in which the sample's deformation under non-oscillating stress is monitored against time or temperature. The temperature and stress profile of the test is programmed. The stress may be compression, tension, flexure or torsion.

In the case of this work a method with three-point flexural test was used to characterise the samples. This was done using TMA from Linseis Messgeräte GmbH. The temperature of furnace was controlled via combine effect of heating elements and liquid nitrogen which is supplied from an external tank. The furnace is air-tightly isolated from the sample chamber. Therefore, the sample is not exposed to potential fast fluctuations, but this also decreases the precision with which the temperature of the sample can be controlled.

Two test profiles were used to characterise the samples. *TMA profile #1* was used for testing the properties of Nitinol before and after different treatments and the testing of "constrained" TWSME. *TMA profile #2* was used for the monitoring of bistable TWSME. Between every step of the procedure the set condition was held for a set amount of time.

TMA Profile #1

The steps of the testing procedure:

1. Raise temperature above A_F at a set rate
2. Decrease temperature significantly below M_F at a set rate
3. Go back to step 1 for a set number of times

The steps of testing for Nitinol properties as well as for "constrained" TWSME were the same. They differed between the exact values and applied force. The exact temperature ranges can be seen from graphs that visualise the results of

TMA. The applied force was 100 mN for testing of OWSME and 80 mN for testing of "constrained" TWSME. The force applied during the testing of TWSME is solely for the purpose of monitoring the shape of the sample. However, force smaller than 80 mN had a high risk of the probe losing contact with the sample.

The temperature heating or cooling rates were set to 3 °C per minute for all tests. The reached temperatures were held for 1 minute.

TMA Profile #2

The steps of the testing procedure:

1. Raise temperature above A_F at a set rate
2. Decrease temperature significantly below M_F at a set rate
3. Raise temperature above T_{trans} to recovery temperature ($T_{R,TMA}$) at set rate - must lie below A_S
4. Decrease temperature below T_{trans} at a set rate
5. Go back to step 1 for a set number of times

The force applied by the TMA machine during this test was solely for the purpose of monitoring deflection. As a result it was set to 80mN as in the case of *TMA Profile #1*.

The temperature heating or cooling rates were set to 3 °C per minute for all tests. Upon heating to $T_{R,TMA}$ the temperature was held for 10 minutes. After reaching other temperatures, they were held for 1 minute.

4.4 Optical Microscope

For the evaluation of laser lines in Nitinol and overall documentation of samples VHX-7000 from Keyence International was used. VHX-7000 allows for measuring surface profile with its "Fine depth decomposition" function.

"Fine depth decomposition" function works by taking pictures of a single area at different focus positions and then combines those to generate profile of the sample surface. It combines them by detecting areas which have high contrast and denotes those as being focused for set position in the direction of z-axis. Based on these principles, to achieve good measurements high magnification was used along with coaxial light.

Chapter 5

Results

5.1 Characterisation of NiTi

DSC and TMA measurements were taken after laser lining and annealing of the Nitinol samples to determine the effects of treatments on mechanical properties. Samples of approximately 20 mm x 5 mm were cut from the bulk material for TMA and small squares of approximately 2 mm x 2 mm were cut for DSC. Laser lined samples were further investigated using optical microscope. Also, some correlations between input parameters of the treatments and their effect were studied. However, due to time constraints the effects were studied only when different results for the induction of bistable TWSME were required.

First, the properties of the virgin bulk material were determined. The result of DSC can be seen in figures 5.1 and 5.2. The result for shape memory foil (figure 5.2) is illustrative of results measured for annealed and laser lined samples. Therefore, only the temperatures A_S , A_F , M_S , M_F , R_S and R_F will be further presented instead of the entire graphs. The result of TMA can be seen if figure 5.3.

The SE foil has very low transformation temperatures for the considered polymers. This means that it will not be possible to use it without further processing. For SM foil we can see clear hysteresis in the transformation temperatures in suitable range for use with the considered polymers (shown in the next section).

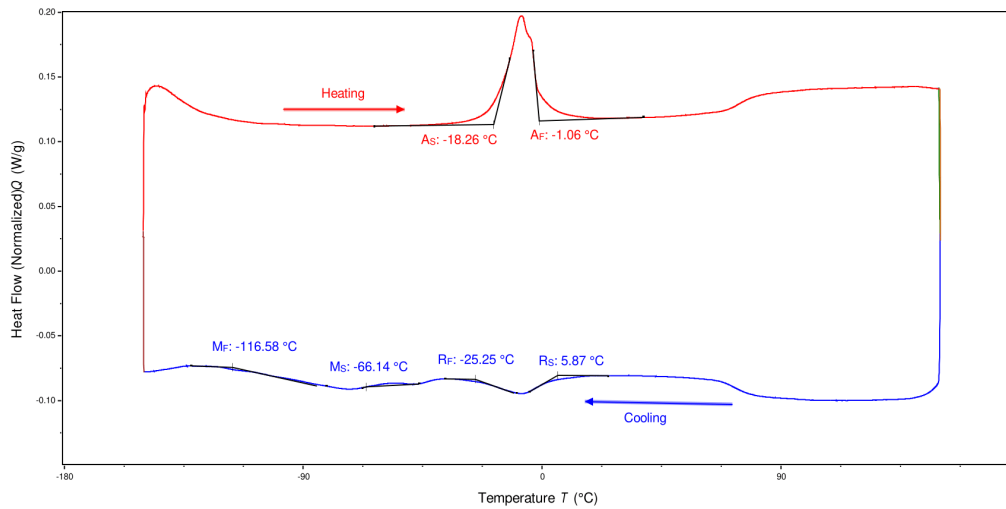


Figure 5.1 DSC of virgin SE foil

For further comparison of TMA with annealed and laser lined samples the focus was not on quantitative result such as deflection. This is because the samples did not always have the same width nor thickness as was the case for laser lined samples. The effects of further processing were followed in terms of change in maximum deflection in martensite and the recovery upon heating and transformation to austenite.

As we can see in figures 5.3b and 5.3a samples achieve greater deflection in martensite over several cycles. The process does not appear to be indefinite and in each cycle the increase in deformation is slightly less than for the previous one. For the recovery upon heating, we see that, compared to the changes in deflection for martensite, the changes in deflection of austenite phase are negligible.

5.1.1 Laser lines

First processing that was studied was laser lining of Nitinol. The input parameters for the laser were spacing of lines, number of passes over the same area and power of the laser. It should be also noted that the laser patterns in samples were not created at the same time. This is important as the laser had to be manually focused to the plane of sample's surface. Although, no measurable effects were detected in samples with same setting created at different times, it is another parameter that potentially changed between the samples.

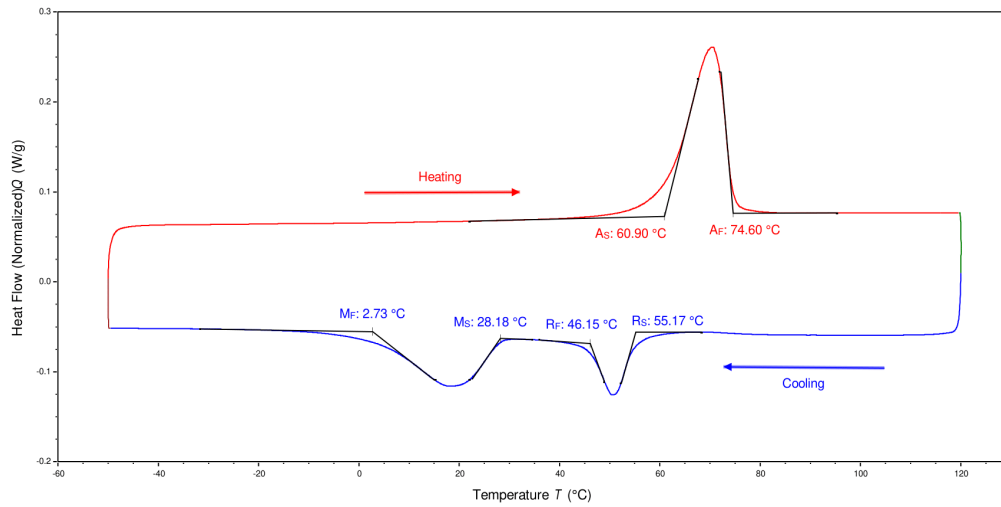


Figure 5.2 DSC of virgin SM foil

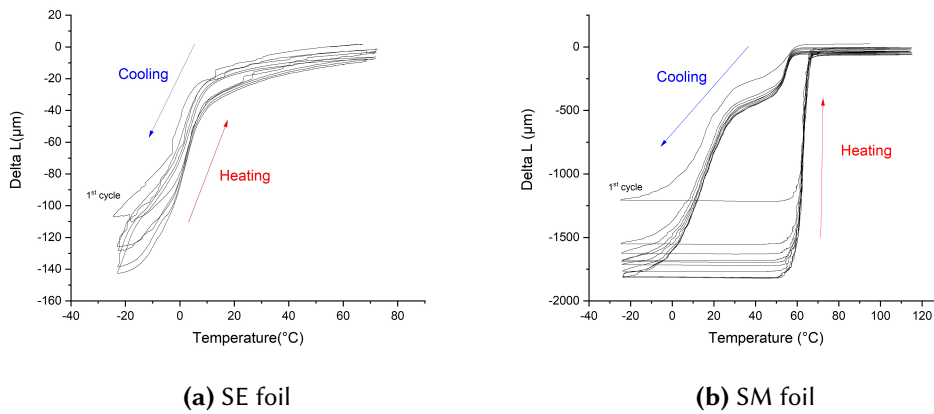


Figure 5.3 TMA of virgin Nitinol samples

The main motivation for creating laser lines in Nitinol was the creation of mechanical interlocking patterns. To evaluate the effect of parameters mentioned above numerous samples were created with power ranging from 10 % to 75 %, number of passes from 1 to 12 and spacing of 0.06 mm up to 0.3 mm. The results were evaluated using optical microscope utilising its "fine depth decomposition" function to determine the depth of created lines. The effect was studied on SM foil. For SE foil only the final chosen setting was tested. It was shown that the result was almost identical to that of the SM foil.

The effect of increasing the power from 45 % to 60 % with 1 pass and 0.3mm spacing can be seen in figure 5.4. The depth of the laser line increased from average of 20 μm to average of 35 μm . The other power settings that were tested were 75 %, 30 % and 15 %. For power of 75 % the depth averaged 45 μm and was deemed too deep as it would remove almost a half of the foil's material. For power setting of 15 % and 30 % the depth was negligible. Power setting chosen for further work was chosen to be 45 %, since laser lining of both surfaces of the samples was considered for the final creation of composite.

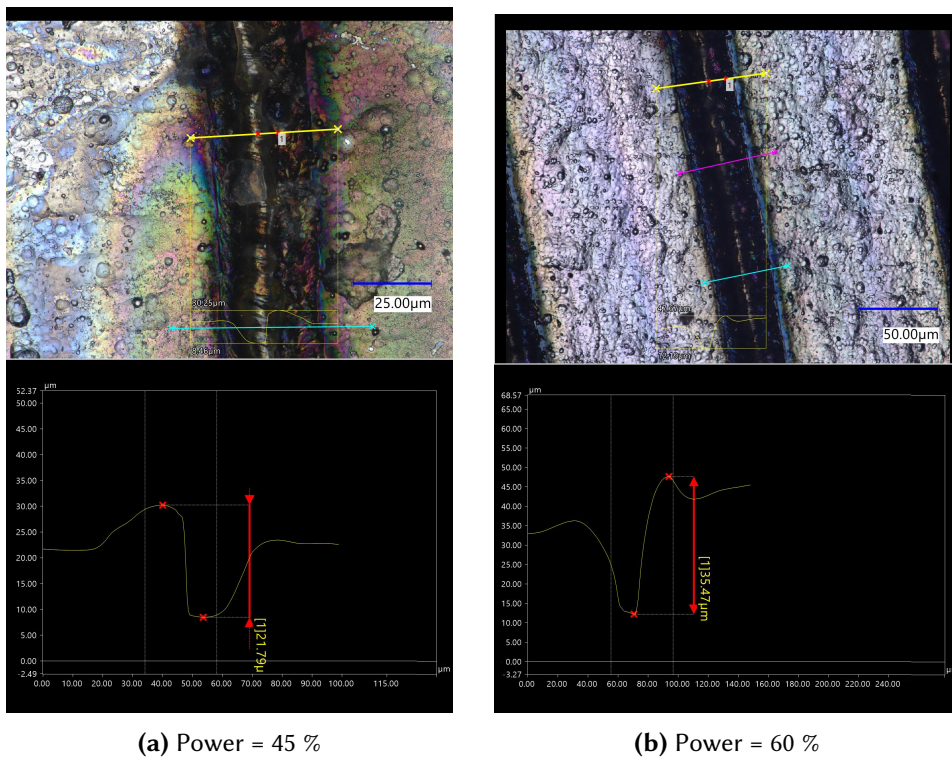
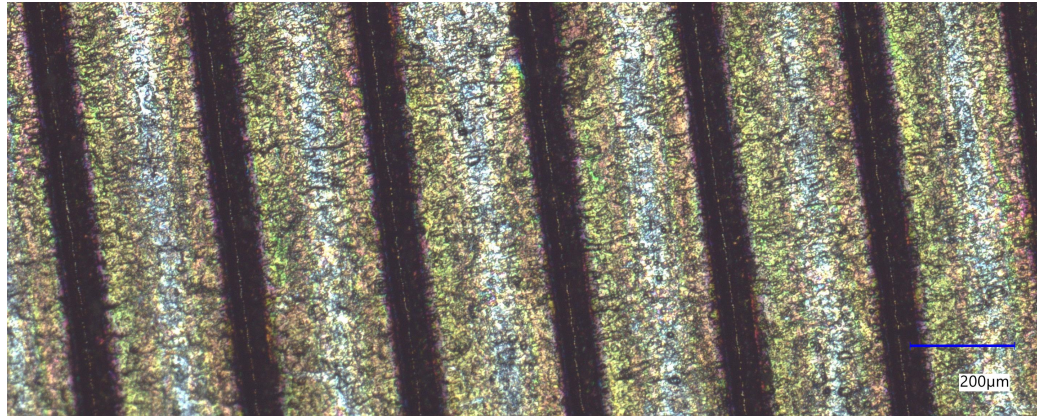
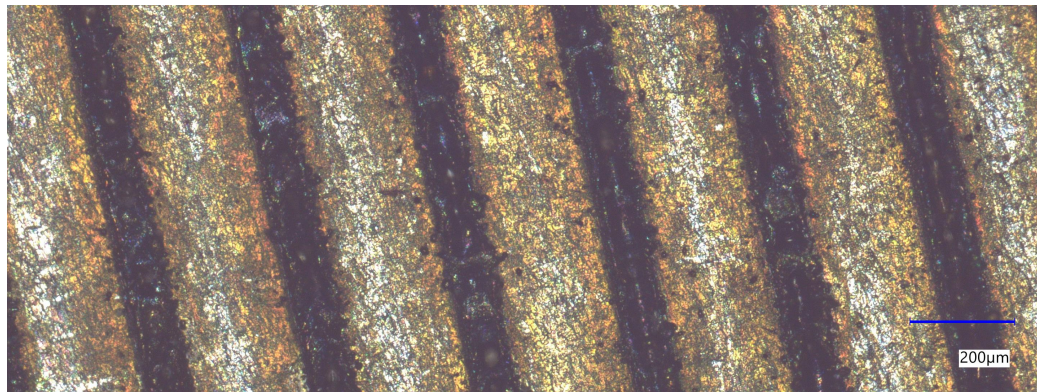


Figure 5.4 Effect of power on the depth of laser lines (number of passes = 1, laser line spacing = 0.3 mm)

The comparison of 1 and 6 passes with power of 45 % and spacing of 0.3 mm can be seen in figure 5.5. The maximum depth of the line did not increase significantly with higher number of passes. However, with more than one passes a deposition of oxide started to form, filling up the laser line. This can be seen as the disappearance of continuous bright lines in the middle of laser lines when comparing the two pictures in figure 5.5. This effect was also seen with only 2 passes albeit to a lesser extent. For this reason, only 1 pass was used for the preparation of surface when creating the composite.



(a) number of passes = 1



(b) number of passes = 6

Figure 5.5 Effect of different number of passes (power = 45 %, line spacing = 0.3 mm)

The effect of laser line spacing was not significant in terms of quality of single line. However, with decreasing spacing the samples would bend and detach from the stainless steel even during the process of laser lining. The length of the sample would also increase the chances of detaching from the surface during the laser lining process. As a result, a spacing of 0.3 mm was chosen for the final preparation of composite.

Majority of samples that were evaluated using optical microscope were then cut and used for DSC testing. The resulting change in transformation temperatures was a shift of up to 2 °C towards higher temperatures for A_F , M_S and R_S and towards lower temperatures for A_S , M_F and R_F . This effect was negligible for the purposes of this thesis.

For TMA testing new samples had to be created. Therefore, only the final chosen setting (power = 45 %, number of passes = 1, line spacing = 0.3 mm) was tested. The result can be seen in figures 5.6a and 5.6b. For SE foil no significant effect was measured. For SM foil the number of cycles to reach repeatable deformation in martensite slightly increased. This effect was negated by further annealing as will be shown below.

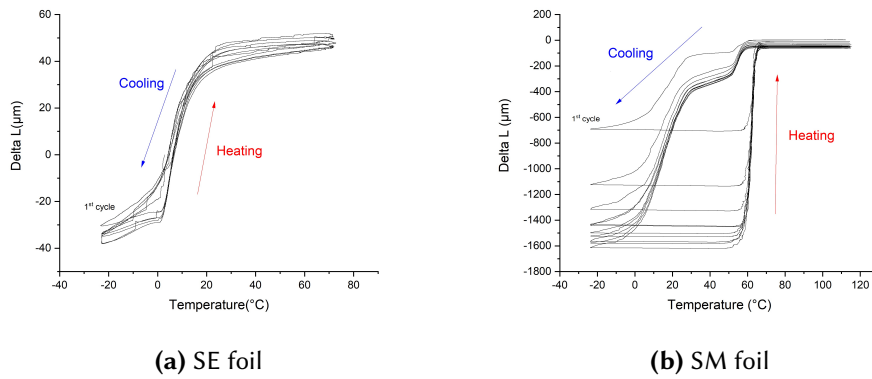


Figure 5.6 Illustrative results of TMA for laser lined samples, 3 point bending with applied force of 100mN

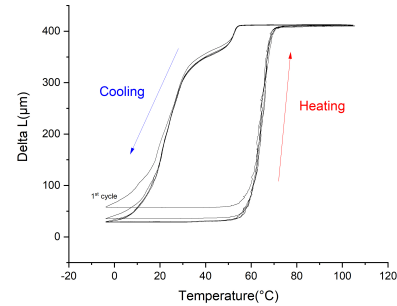
5.1.2 Annealing

Next the effect of shape setting by annealing on the transformation temperatures and mechanical properties was studied. The samples were secured in aluminium form with set radius of curvature as can be seen in figure 5.7a. Aluminium has a melting temperature of around 600 °C. Therefore, the temperature for annealing had to be kept significantly lower than this and was chosen to be 400 °C. The effect of different annealing times from 2 to 18 hours was studied.

Upon annealing, SE foil lost its super elastic properties and transformed into shape memory foil with transformation temperatures of $A_S = 39$ °C, $A_F = 50$ °C, $R_S = 45.5$ °C, $R_F = 39$ °C, $M_S = -5.5$ °C and $M_F = -45$ °C. This range was not suitable for further use in composite. Therefore, the SE foil was determined to be unusable for the purpose of inducing bistable TWSME as it could not be shape set or didn't have suitable transformation temperatures neither prior nor after shape setting. Further only SM foil was considered.



(a) Sample in bending mould after annealing



(b) TMA of SM foil sample annealed at 400°C for 2 hours

Figure 5.7 SM foil annealing

Annealing SM foil sample not only changed its parent phase but also altered its transformation temperatures. The effect was more severe for longer annealing times as can be seen in table 5.1. The longer annealing time has an effect of decreasing the hysteresis of the sample. This is undesirable as it decreases the viable temperature range for T_{trans} of polymer. For this reason, a sample annealed only for 2 hours was created. This sample also had a new parent shape with no measurable difference in quality from the other 2 samples.

annealing time	A_S (°C)	A_F (°C)	R_S (°C)	R_F (°C)	M_S (°C)	M_F (°C)
0 hours (virgin)	61	74.5	55	46	28	2.5
2 hours	61	75	55.5	49.5	32.5	9
3 hours	60.5	76	55.5	49	31.5	9.5
18 hours	59	78.5	54	48	34	11

Table 5.1 Transformation temperatures after different annealing times

The effect of annealing on TMA can be seen in figure 5.7b. The annealed sample had a reduced number of cycles prior to achieving repeatable strain at the martensite phase. It also widened the temperature range at which the sample was recovering its strain while transforming into austenite, which is coherent with the result obtained from DSC. Similar results were observed for samples that were annealed for longer times. Overall, an annealing time of 2 hours at 400 °C was most suitable for the creation of a composite and was selected for further use.

5.1.3 Laser Lines Combined With Annealing

Lastly, the effect of combining both laser lines and annealing was studied. The settings that were tested were only the ones which have been shown above to be most suitable for the preparation of composite. The laser lining parameters were power = 45 %, number of passes = 1 and line spacing = 0.3 mm. The samples were annealed after creating laser lines for 2 hours at 400 °C with radius of curvature of 15 mm. In addition to configuration with one surface being laser lined, both surfaces were laser lined and their mechanical characteristics tested.

The results showed that after annealing the alteration of Nitinol's properties by laser lining were negligible. TMA was almost identical to the sample with no laser lines that was annealed at the same setting. Slight difference was in the result of DSC. The resulting transformation temperatures were $A_S = 62^\circ\text{C}$, $A_F = 75^\circ\text{C}$, $R_S = 55.5^\circ\text{C}$, $R_F = 49^\circ\text{C}$, $M_S = 31^\circ\text{C}$, $M_F = 9^\circ\text{C}$.

5.2 Characterisation of Polymers

First DSC of polymers was performed to get a rough estimate of their transformation temperature (T_{trans}). For crystalline polymers small pieces of filament were annealed. TPU was not measured as it does not have reported transformation temperature of interest for the studied temperature range. For PCL small pieces of filament were cut for the experiment. The DSC of HD PLA in figure 5.8 is illustrative of the result for PLLA. CoPa did not show any distinct peaks during the measurement.

The measured transformation temperature for HD PLA was 60 °C and PLLA 62 °C. The transformation temperature of CoPa was not detected. The melting and solidification temperatures of PCL had a certain amount of hysteresis with peaks of significant width. The resulting measured temperatures were $T_{M,S} = 55.5^\circ\text{C}$, $T_{M,F} = 62.5^\circ\text{C}$, $T_{S,S} = 40^\circ\text{C}$ and $T_{S,F} = 28.5^\circ\text{C}$.

5.2.1 Testing the Existence of OWSME in Polymers

To test the existence of OWSME, 3D printed and annealed stripes of PLLA, HD PLA and CoPa were tested for shape memory capability using *DMA Profile #1* described in *Methods of characterisation*. The temperatures $T_{R,DMA}$ and T_D were set to be 70 °C and 100 °C respectively. ϵ_D was adjusted in reaction to the behaviour of samples.

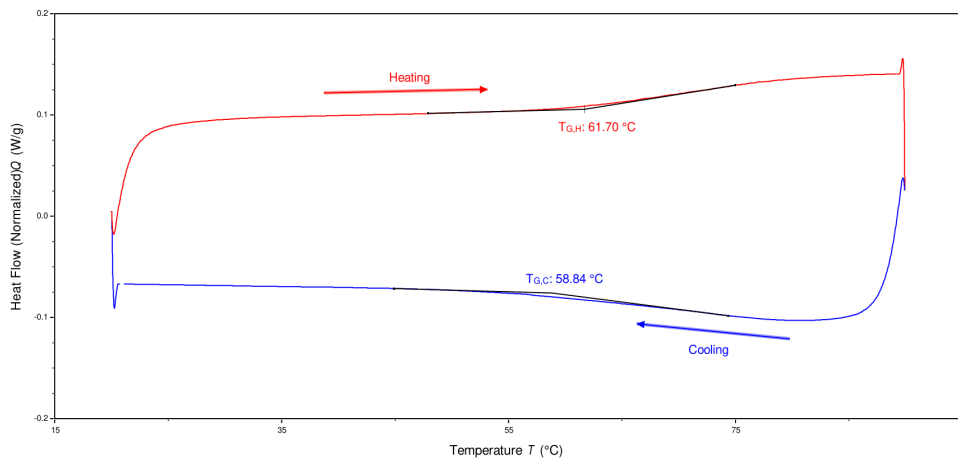


Figure 5.8 DSC of annealed HD PLA

For PLLA the test was executed multiple times. However, each time the sample broke during the first cycle while being stretched to ϵ_D even when the strain was low as 4 %. The sample did not snap at a particular moment but rather developed a failure at the edge that then progressed through the body of the sample. The entire process took around 5 seconds based on the stress data obtained.

After these attempts an unannealed sample was tested to compare its behaviour to the previous ones. This time the sample did not break but rather stretched even with only the preload force applied. The resulting comparison of failure between the annealed and unannealed sample can be seen in figure 5.10.

Sample of HD PLA did develop a neck, but it did not break. This was consistent over the two test that were performed for strain of 50 % and 30 %. For strain of 30 % the fixity and recovery ratios were about 90 % and 80 % respectively for the five performed cycles. However, during the first cycle the recovery ratio was only 27 % due to the formation of the neck. For the testing with 50 % strain only two cycles were performed and therefore the recovery and fixity ratios were not determined.

The CoPa samples did not break or develop a neck during any of the tests that were performed with the 3D printed samples. They were tested with strains of up to 50 %. For strain of 20 % 6 cycles were performed. The fixity and recovery ratios were approximately 97 % and 95 % although during the first cycle the recovery ratio was only 18 %. It was also found that the recovery during the first cycle

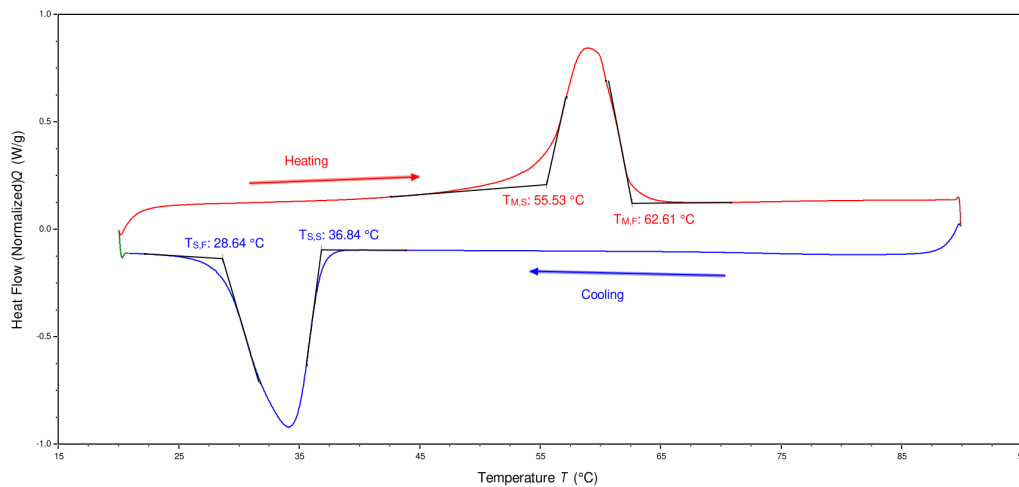


Figure 5.9 DSC of PCL

was reduced significantly when the $T_{R,DMA}$ was set to 65 °C instead of 70 °C from 18 % to less than 10 % percent of strain recovered during the first cycle. The subsequent recoveries remained relatively unchanged.

For the polymer blend several ratios have been tested. The tested mixtures were labelled TPUX&PCLY where X and Y are numbers. These numbers represent the mass fraction of polymer in the blend (X for TPU and Y for PCL). The tested mixtures were TPU90&PCL10, TPU80&PCL20, TPU60&PCL40, TPU40&PCL60, TPU20&PCL80 and TPU10&PCL90. The samples were tested in DMA 850 using the *DMA Profile #1* with $T_D = 80$ °C, $T_{R,DMA} = 60$ °C and $\epsilon_D = 10$ %. Mixtures TPU40&PCL60, TPU20&PCL80 and TPU10&PCL90 stretched under the preload force of 0.01 N and were therefore not considered for further work. Other ratios did perform well and were further characterised.

Overall, after the initial evaluation of shape memory properties of considered polymers, PLLA and blends of TPU and PCL with less than 60 % of TPU were not further studied.

5.2.2 Evaluation of Shape Memory Properties

The first sample to be tested was HD PLA. During first four attempts the sample broke in brittle manner within the first two cycles with strains of 50 %, 20 %, 5 % and 3 %. This was caused by two main factors. First, small bubbles were present in the body of samples. Second, due to higher crystallinity of the sample



Figure 5.10 3D printed samples of polymers after testing, starting from left: PLLA annealed, PLLA unannealed, HD PLA, CoPa and TPU60&PCL40

Name of polymer	$\sigma_R = 0$ MPa		$\sigma_R = 0.1$ MPa		T_{fix} (°C)	T_R (°C)
	R_{fix} (%)	R_R (%)	R_{fix} (%)	R_R (%)		
TPU60&PCL40	94	99	97	94	19.5	56
TPU80&PCL20	87	99	92	95	18.5	52.5
TPU90&PCL10	83	96	83	96	15.5	51
CoPa	82	97	not measured		60	64
HD PLA	82	97			100-10	63.5

Table 5.2 Measured parameters describing the shape memory behaviour of studied polymers, σ_R denotes applied stress upon recovery

it did not neck around the bubble like the 3D printed sample would. Fifth attempt with strain of 3 % was successful in completing three full cycles. The resulting parameters can be found in table 5.2. This time the samples broke with no bubble as a cause of stress concentration. Nor were any bubbles found in the body of the sample during subsequent investigation. For this reason, HD PLA was not further considered for the creation of composite.

Second polymer to be tested was CoPa. This polymer performed well with *DMA Profile #1* with $T_D = 100$ °C, $T_{R,DMA} = 70$ °C and $\epsilon_D = 5$ %. The resulting parameters can be seen in table 5.2. However, its recovery temperature (T_R) was determined to be 64 °C. It was also found at this time that the effect of annealing with and without laser lining did not increase the austenite transformation tem-

perature but rather decreased it. This meant that the transformation temperature (T_{trans}) of CoPa lied above the A_S . For this reason, the characterisation of CoPa was not further pursued and the sample wasn't used for the creation of bistable TWSME composite.

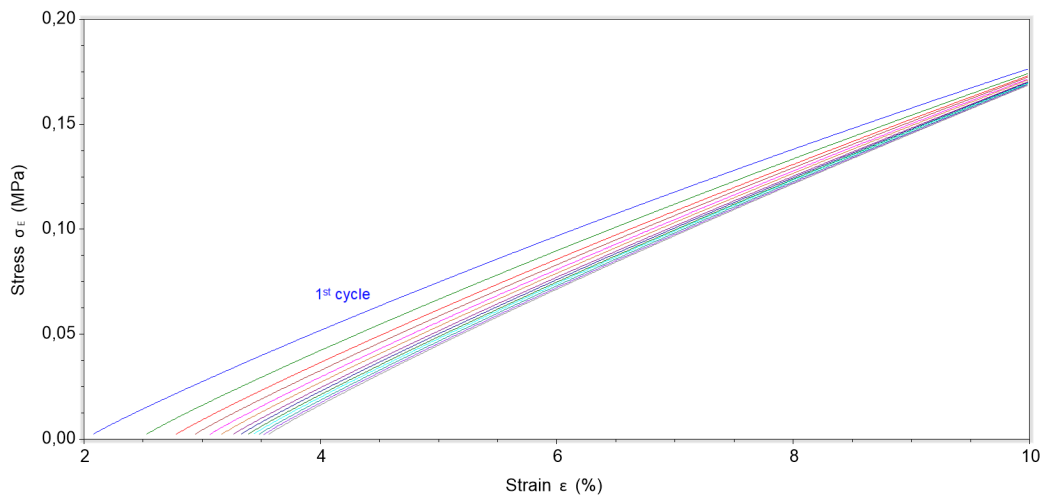


Figure 5.11 SMP characterisation - deforming at T_D

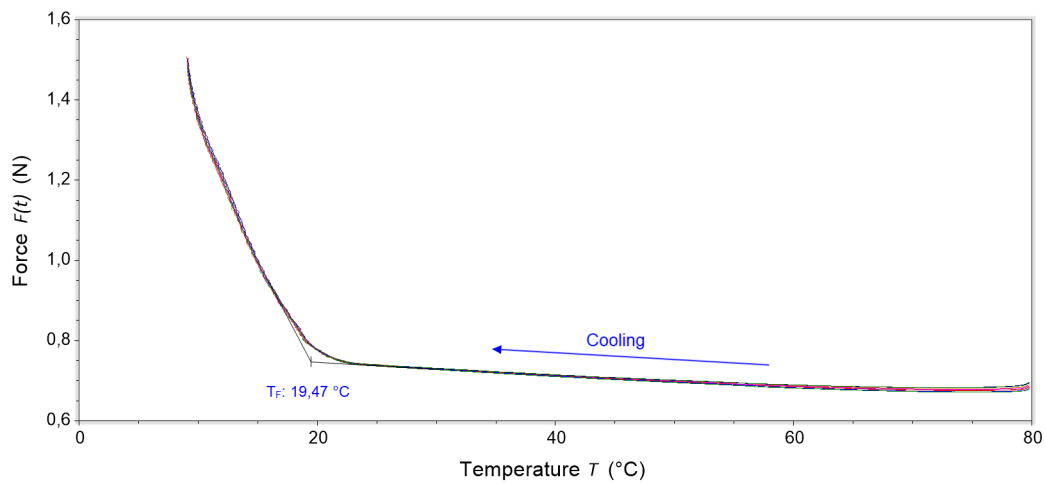


Figure 5.12 SMP characterisation - cooling at ϵ_D

Next, TPU60&PCL40, TPU80&PCL20 and TPU90&PCL10 were tested. The behaviour of these samples was characterised both using *DMA Profile #1* and *DMA Profile #2* with $T_D = 80\text{ }^\circ\text{C}$, $T_{R,DMA} = 60\text{ }^\circ\text{C}$ and $\epsilon_D = 10\%$. The load upon recovery between the profiles increased from approximately 10^{-3} MPa to 0.1 MPa . To illustrate testing profiles the resulting graphs of several steps for *DMA Profile #1* of TPU60&PCL40 can be seen in figures 5.11 through 5.14. The resulting parameters can be seen in table 5.2.

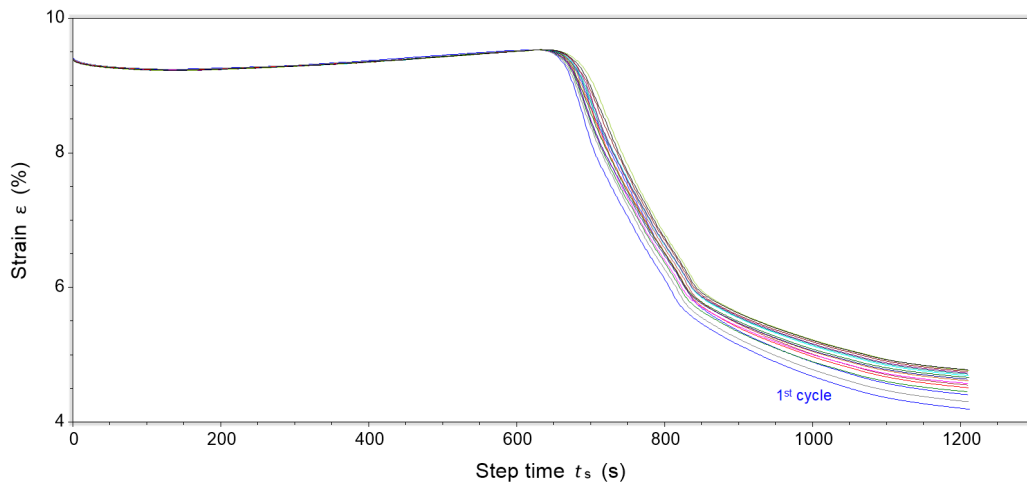


Figure 5.13 SMP characterisation - recovery - time dependence

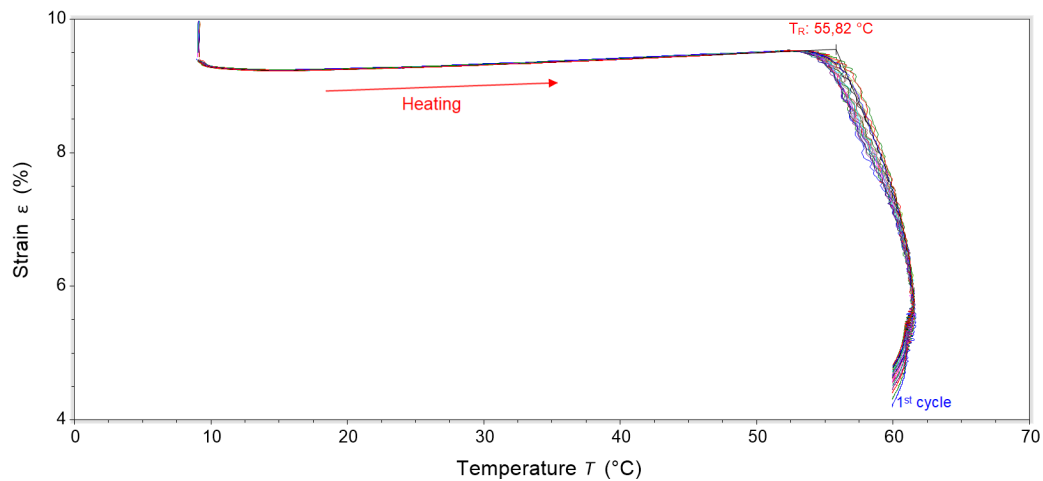


Figure 5.14 SMP characterisation - recovery - temperature dependence

As shown above, Nitinol sample is able to deform even below 20 °C (see Figure 5.7b). Therefore, although the fixation temperature (T_{fix}) of TPU&PCL blend is lower than M_S of Nitinol, significant strain can be still fixed by this polymer. Based on these results, the blend of 60 % of TPU and 40 % of PCL was selected as the most promising polymer blend for preparation of composite.

5.3 Characterisation of Composite

As a result of the previous research only blend of TPU and PCL was deemed viable for the creation of bi-stable TWSME composite. The chosen polymer blend was TPU60&PCL40 as it has the highest solidification temperature during programming of deformed shape of the polymer.

For preparation of Nitinol a stripe of dimensions 40 mm x 5 mm was laser lined on both surfaces with settings of power = 45 %, number of passes = 1 and line spacing = 0.3 mm. The sample was then annealed at temperature of 400 °C for 2 hours with a set radius of curvature = 15 mm.

The tested composite sample was prepared with the first iteration of the process described in *Notes on the Preparation of composite*. The upper body of polymer had large voids within it. This allowed the probe of TMA to be directly placed on the Nitinol stripe. Therefore, there was no risk of the measurement being plagued by different penetration depths of the probe into the polymer with changing temperature. The sample was tested with the *TMA Profile #1* with $T_{R,TMA} = 60$ °C and applied force of 80 mN for total of 6 cycles. The resulting graph can be seen in figure 5.15.

The composite does exhibit bistable TWSME of 10 µm. In graph we can also see certain peaks that correspond to transformations in the polymer blend as well as the transformation temperatures of Nitinol.

After testing it was found that the bottom polymer detached from the NiTi strip (bottom side reeferers to polymer in tension and top side to the polymer in compression). This can be seen in figure 5.16a. Two possible causes of delamination were identified:

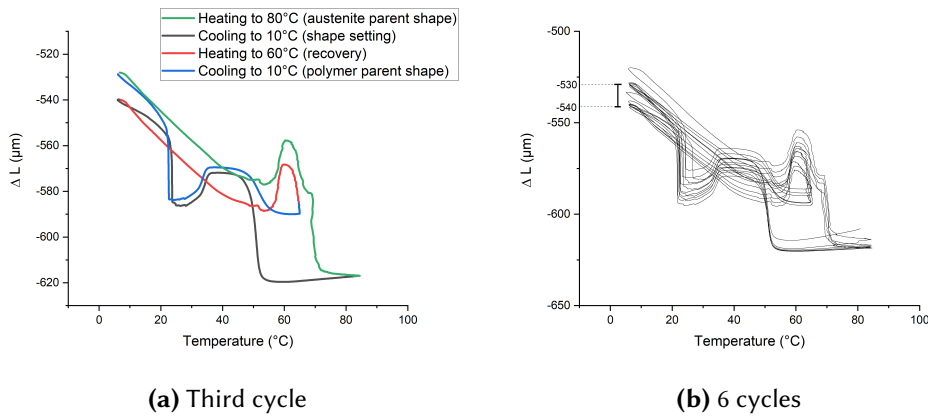


Figure 5.15 First six cycles of TMA testing of TPU60&PCL40 + Nitinol composite

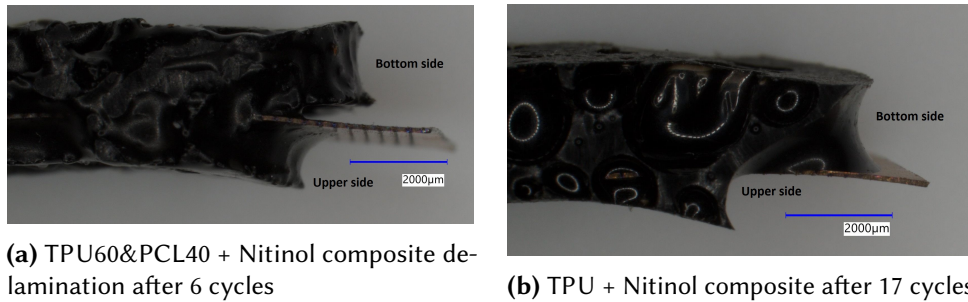


Figure 5.16 Evaluation of delamination in composites

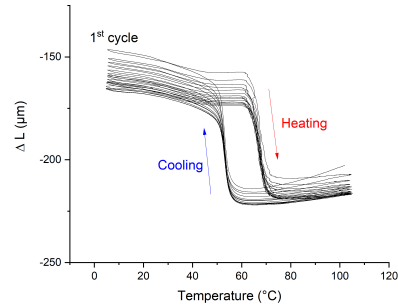
1. When the PCL component in the polymer blend melts it causes the entire blend to detach from the Nitinol
2. The delamination is caused by the insufficient strength of the bond between the Nitinol stripe and TPU

A composite of pure TPU and Nitinol was prepared to differentiate which of the possibilities described above caused the delamination. The composite was prepared in the same way as the TPU60&PCL40 + Nitinol composite.

The resulting sample can be seen in figure 5.17a. It has significantly higher difference in the thickness of attached TPU on both sides and similar structure of voids as that of the TPU60&PCL40 composite. The resulting TMA can be seen in figure 5.17b where the "constrained" TWSME can be seen.



(a) Side view of TPU + Nitinol composite after TMA testing

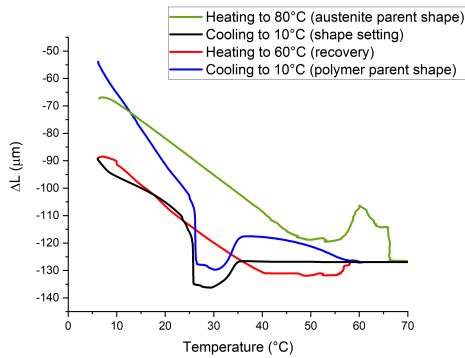


(b) 17 cycles of TMA Profile #1

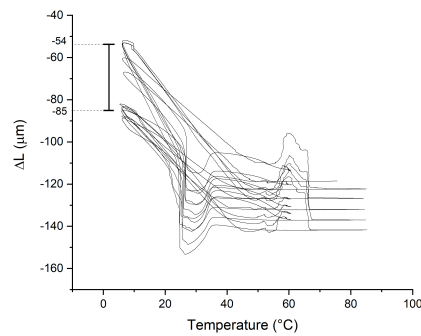
Figure 5.17 TPU + Nitinol composite results

No delamination after 17 cycles was seen as can be seen in figure 5.16b. Therefore, it was concluded that the delamination was caused by the melting of PCL in polymer blend.

During the initial six cycles of TMA, we can see that the temperature fluctuates up to 64 °C which is above A_S . Therefore, six more cycles of TMA Profile #2 were executed with force of 80 mN and $T_{R,TMA} = 56$ °C. The resulting data can be seen in figure 5.18. It should be noted that the first and second testing of TPU60&PCL40 + Nitinol composite was done about 24 hours apart. During this time the sample was kept at ambient room conditions.



(a) Third cycle



(b) 6 cycles

Figure 5.18 Second six cycles of TMA testing of TPU60&PCL40 + Nitinol composite

After the second test no further delamination of polymer blend from Nitinol was detected. Also, higher difference in deformation was recorded of up to 31 μm.

Chapter 6

Discussion of Results

6.1 Nitinol

Two types of NiTi foil were considered at the beginning of the work - shape memory and super elastic foil. It was found that it is not possible to change the parent shape of the SE foil and its transformation temperatures to be compatible with any of the tested polymers. Therefore, only shape memory foil is discussed below.

Parameters for preparation of Nitinol were determined. The power of the laser for the preparation of final composite was set to be 45 %. This created valleys of about 20 μm . The target was to create laser lines on both surfaces of the Nitinol stripe. Combined with the information that the thickness of Nitinol was 100 μm this depth was deemed acceptable. For higher power too much of the material would be removed and with less power the depth was less than 10 μm and was deemed insufficient. A single pass over the surface of the sample was chosen. Subsequent passes caused the valley to start filling up with oxides. This negated any additional control over the depth of the line that might have been provided by this parameter. Laser line spacing was chosen to be 0.3 mm. Decreasing the spacing would cause complication during the preparation especially with longer samples.

For annealing, the temperature was limited by the melting temperature of the forms which were made from aluminium with melting temperature around 600 °C. The annealing temperature was set to be 400 °C. The sample was annealed for 2 hours which was sufficient to shape set the sample with a radius of curvature of 15 mm. Further annealing was not found to improve the shape setting of Nitinol and it decreased the hysteresis window. The transformation temperatures after

annealing and laser lining were found using DSC and were $A_S = 62^\circ\text{C}$, $A_F = 75^\circ\text{C}$, $R_S = 55.5^\circ\text{C}$, $R_F = 49^\circ\text{C}$, $M_S = 31^\circ\text{C}$, $M_F = 9^\circ\text{C}$. The OWSME effect of Nitinol was not severely damaged during this process. The maximum deformation at martensite decreased but the more important recovery of deformation upon heating to austenite remained unchanged.

6.2 Polymers

Potential shape memory polymers compatible with Nitinol for the creation of bistable TWSME composite were investigated. They are listed in table 6.1. Rough estimates of their transformation temperatures were made using DSC. The measure T_{trans} were 60°C for HD PLA and 62°C for PLLA. Transformation temperature of CoPa was not detected. The melting and solidification temperatures of PCL had a certain amount of hysteresis with peaks of significant width. The resulting measured temperatures were $T_{M,S} = 55.5^\circ\text{C}$, $T_{M,F} = 62.6^\circ\text{C}$, $T_{S,S} = 39.8^\circ\text{C}$ and $T_{S,F} = 28.6^\circ\text{C}$. The $T_{S,F}$ lies below M_S of processed Nitinol. However, it refers to the finish solidification temperature therefore the effect of this should be negligible. Next, the polymers were tested for the existence of OWSME.

Polymer	Result of testing
PLLA	Discarded after initial testing due to high crystallinity that caused it to break in brittle manner
HD PLA	Discarded during evaluation of OWSME due to high crystallinity and high recovery temperature (T_R)
CoPa	Discarded due to recovery temperature (T_R) being higher than A_S of processed Nitinol
TPU10&PCL90 TPU20&PCL80 TPU40&PCL60	Discarded due to sagging under the preload force of 0.1 N when heated above melting temperature of PCL
TPU60&PCL40	Was selected for the preparation of bistable composite
TPU80&PCL20 TPU90&PCL10	Discarded due to high fixation temperature (T_{fix})

Table 6.1 Studied polymers and discussion regarding their use in bistable composite

The PLLA polymer was discarded due to its high crystallinity which caused it to break in a brittle manner during SMP testing. A potential solution to this would be to change the annealing parameters of the sample to decrease the resulting crystallinity. This has been shown to be possible in [16]. The difference, in this case, is that after annealing the sample could be annealed further during cycling. The deciding factors would be the amount of crystallinity achieved at A_F and whether the crystallisation would continue indefinitely with cycling.

A similar problem was confronted with HD PLA when the sample was made by pressing in hot press. The samples were annealed at temperatures above A_F . This implies that the sample would not anneal further upon cycling. Altered pressing process was envisioned to solve the problem of high crystallinity from slow cooling:

1. Melt samples in hot-press and press them to the desired shape
2. Upon cooling remove the samples from the hot press
3. Let the samples cool in ambient air or quench them in water to speed up the cooling process
4. Anneal the samples at a set temperature for a set time

This process would closer imitate that of 3D printing and allow the crystallinity to be mainly set by annealing conditions. Regardless of the complications with brittle behaviour three full cycles were achieved and the parameters of HD PLA were determined. The fixity ratio (R_{fix}) was measured to be 82 %, recovery ratio (R_R) 97 % and recovery temperature (T_R) 63.5 °C. The fixation temperature was not a single value as the polymer appeared to start fixating the deformation upon cooling. It should be noted that to determine these values the strain ϵ_D had to be reduced to 3 %.

The CoPa polymer fared well in both initial testing and evaluation of shape memory properties. The polymer never broke during the cycling process nor did it develop a neck. 20 cycles of *DMA Profile #1* were performed with $\epsilon_D = 5 \%$, $T_D = 100 \text{ °C}$ and $T_{R,DMA} = 70 \text{ °C}$. The parameters were determined to be $R_{fix} = 82 \%$, $R_R = 97 \%$, $T_{fix} = 60 \text{ °C}$ and $T_R = 64 \text{ °C}$. Unfortunately, the recovery temperature lies above the A_S of the Nitinol after processing. Therefore, the CoPa polymer was not further studied.

After initial testing TPU60&PCL40, TPU80&PCL20 and TPU90&PCL10 were chosen for further investigation. Blends with less than 60 % TPU were not found suitable as they stretched under the preload of 0.01 N when heated above melting temperature of PCL. The suitable blends were first tested with at least 6 cycles *DMA Profile #1* with $\epsilon_D = 10 \%$, $T_D = 80 \text{ }^\circ\text{C}$ and $T_{R,DMA} = 60 \text{ }^\circ\text{C}$. Their recovery temperature was below A_S and they showed recovery ratios of up to 99 % which is higher than reported in [8]. This is most likely by the lower ϵ_D which was 30 % in the case of [8]. Subsequently the blends were tested with *DMA Profile #2* and load of 0.1 MPa with same temperature and strain parameters. The recovery ratios decreased to approximately 95 % and fixity ratios either slightly increased or did not change.

Overall, only complication arose with fixity temperature (T_{fix}) which was found to be slightly lower than the M_S of Nitinol. Blend of TPU60&PCL40 was chosen for the preparation of the composite since it was found to have the highest fixity temperature of tested blends at 19.5 °C. The parameters of TPU60&PCL40 were $T_{fix} = 19.5 \text{ }^\circ\text{C}$, $T_R = 56 \text{ }^\circ\text{C}$, $R_{fix} = 94 \%$ and $R_R = 99 \%$ without load upon recovery and $R_{fix} = 97 \%$ and $R_R = 94 \%$ with load of 0.1 MPa upon recovery.

6.3 Composite

The composite tested for bistable TWSME was prepared with the first iteration of the process as described in subsection *Notes on the Preparation of Composite*. The sample was tested twice with *TMA Profile #2* with force of 80 mN. During the first test the $T_{R,TMA}$ was set to 60 °C and during second to 56 °C. It was found that the composite recovered from up to 50 % of its deformation during its transformation to R-phase which could not be fixated by the polymer. Also, the fixation temperature (T_{fix}) of the TPU60&PCL40 blend was below that of M_S , therefore further deformation was recovered prior to fixation. Regardless of the issues the sample did exhibit bistable TWSME during both measurements. The first 6 cycles exhibited difference in bending of 10 µm and showed distinct peaks that correspond to the transformation temperatures of Nitinol and polymer blend. This is most likely caused by changes in volume during these processes as the polymer thickness was not same on both sides of the Nitinol stripe. It was also found that the polymer detached on the ends of the Nitinol stripe on the tension side of the composite.

The second 6 cycles showed serious change in the behaviour of the composite. This might be caused partially by the lowering of $T_{R,TMA}$ which resulted in the machine accurately achieving 60 °C. This resulted in the sample achieving higher

difference in deformation of up to 31 μm . It is also possible that the change in difference of deformation is due to higher moisture content in the sample since it was kept at ambient room conditions for 24 hours between the tests. The delamination on the tension side of the composite did not progress any further. This suggests that the delamination occurs within the first few cycles. The possible causes of this were the melting of PCL component in the blend or insufficient bonding strength between TPU and Nitinol.

A sample of TPU + Nitinol was prepared using the first iteration of the process described in *Notes on the Preparation of Composite*. This was to test which of the possible causes for delamination described above was correct. The sample performed well with *TMA profile #1* with force of 80 mN and exhibited "constrained" TWSME with deflection of about 60 μm . The difference in remembered shape remained unchanged within the 17 cycles performed. However, the absolute deformations did change and seemed to be approaching a constant value. This is most likely due to the degradation of TPU.

Upon removing the sample from TMA no delamination was found. This suggests that the delamination in blended composite was caused by the melting of PCL that damages the interface between layers.

It should be noted that the force generated by TMA machine did act against the recovery of polymer in both bistable and constrained composite. The maximum potential deformation could not be reached as a result.

Conclusions

In this bachelor, the results of research activities carried out during the experimental period at the Institute of Physics of the Czech Academy of Sciences are presented. The aim of these activities was to prepare a bistable two-way shape memory composite utilising Nickel-Titanium alloy and shape memory polymer. To this end the research was divided into several parts - the processing of Nitinol foil without severely damaging its shape memory property, the identification, preparation and testing of suitable shape memory polymers and finally the preparation and testing of composite.

First, the procedure to prepare Nitinol for use in the composite material was developed. The parameter for laser lining were tailored to create clear valleys in the surface of Nitinol with an average depth of 20 μm with spacing of 0.3 mm. The subsequent annealing at 400 $^{\circ}\text{C}$ for 2 hours successfully fixated a curved parent shape with radius of 15 mm into the parent shape. The resulting sample had reduced deformation upon loading in martensite and shifted transformation temperatures but its ability to recover deformation upon heating remained unchanged.

Second, the potential shape memory polymers were prepared and tested. The tested polymers were PLLA, HD PLA, CoPa and blend of TPU and PCL at different ratios. The polymer chosen for the preparation of composite was blend of 60 % TPU and 40 % PCL by weight. This blend exhibited high recovery ratio (R_R) of 99 % without applied load and 94 % with applied stress of 0.1 MPa upon recovery. It also had the highest fixation temperature (T_{fix}) of 19.8 $^{\circ}\text{C}$

Lastly, the final composite was prepared using a hot press. The polymer in the composite had a severe number of voids. However, this did not seem to affect the polymer's ability to bind to Nitinol. The sample was tested in TMA using *TMA Profile #2* with 80 mN of force and $T_{R,TMA} = 60$ $^{\circ}\text{C}$. It was found that most of the strain in parent shape of austenite was recovered during the transformation to R-phase. Also, since the $M_S \approx 28$ $^{\circ}\text{C}$ the composite continued further to recover its polymer parent shape prior to the fixation of austenite

parent shape. Regardless of this the composite still exhibited bistable TWSME with repeatable difference in deformation of 10 μm during its first testing with 6 cycles. Delamination of the polymer on the tension side of composite was found after the testing. This was attributed to the PCL component of polymer blend melting and damaging the interface. This was determined after sample of TPU + Nitinol composite showed no signs of delamination after 17 cycles. Further 6 cycles with $T_{R,TMA} = 56\text{ }^\circ\text{C}$ of bistable TWSME composite showed increase in the difference of deformation up to 31 μm and no further delamination.

Future work

For future development, the aim will be to improve the compatibility of transformation temperatures of Nitinol and shape memory polymer by removing R-phase or changing the transformation temperature of Nitinol or by changing the transformation temperature (T_{trans}) of polymer to lay between R_S and A_S . The transformation temperature of Nitinol can be changed by the addition of metals into NiTi. Commonly used metal to this end is Hf which significantly widens the hysteresis curve of NiTi potentially making CoPa compatible for the use in bistable composite as well. On the side of the polymer a mixture of 50 % TPU and 50 % PCL can be tested as it is likely to have higher T_{fix} based on the obtained data. Also, even if testing of shape memory property might not be possible for samples with less than 60 % TPU, they might be still usable for the creation of bistable TWSME composite and are likely to have higher fixation temperatures.

Also, interface between the two constituents can be further improved. There have been several approaches envisioned to this end. The patterns and parameters of laser line can be further tailored to improve the adhesion of the polymer. Also, techniques utilising glue or other form of binding agent can be used to create the composite. This would also allow for easier manufacture process as the sample of TPU&PCL could be made separately and then attached to the Nitinol. Further to eliminate the problem of melting PCL along the Nitinol-polymer interface, it might be possible to create gradient of PCL concentration within the body of polymer. This would allow for pure TPU to be present at the interface with blend being present at the outer surfaces of the composite.

Further work can also be done on the preparation process of the composite. It is desirable to remove the individual plates as they move during the placement of NiTi strip and further complicate the process of preparation. To solve this a two-piece holder could be designed to hold the NiTi sample in straight shape. It could also provide control over the total thickness of the sample. Model presented in [17] could be used to calculate the desirable thickness of polymers.

Finally, the testing method of TWSME effect can be further improved. Testing via TMA adds another force that acts during testing. To avoid this, the sample can be secured at one end with the other allowed to move freely. Then the sample would be cycled through the same temperature profile as *TMA Profile #2*. Camera with evaluation software could be used to monitor the samples behaviour and evaluate its deflection free of any load.

Nomenclature

OWSME - One-way shape memory effect
TWSME - Two-way shape memory effect
NiTi - Nickel Titanium alloy
SM foil - NiTi foil exhibiting OWSME
SE foil - NiTi foil exhibiting superelastic behaviour
 A_S - Austenite (transformation) start temperature
 A_F - Austenite (transformation) finish temperature
 R_S - R-phase (transformation) start temperature
 R_F - R-phase (transformation) finish temperature
 M_S - Martensite (transformation) start temperature
 M_F - Martensite (transformation) finish temperature
 T_{trans} - Transformation temperature in the process of OWSME in polymers
 T_G - Glass transformation temperature
 T_M - Melting temperature
 R_{fix} - Fixity ratio of polymer
 R_R - Recovery ratio of polymer
 ϵ_D - Deformation strain in testing OWSME of polymers
 ϵ_F - Fixated strain in OWSME of polymers
 ϵ_R - Recovered strain in OWSME of polymers
 T_F - Fixating temperature in OWSME of polymers
 T_R - Recovery temperature in OWSME of polymers
PLLA - Poly L-lactic acid
HD PLA - Heat deflection polylactic acid
CoPa - Mixture of PA6 and PA6.6
TPU - Thermoplastic polyurethane
PCL - poly(ϵ -caprolactone)
DSC - Differential scanning calorimetry
DMA - Dynamical mechanical analysis
TMA - Thermomechanical analysis
 T_D - Deformation temperature in *DMA Profile #1/#2*
 $T_{R,DMA}$ - Temperature reached for recovery of polymer in *DMA Profile #1/#2*

$T_{R,TMA}$ - Temperature reached for recovery of composite in *TMA Profile #2*

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