IMPROVING THE MECHANICAL PROPERTIES OF BRAIDED SHAPE MEMORY POLYMER STENTS BY HEAT SETTING

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Abstract:

The aging population is one of the biggest challenges of the 21st century and so is the subsequent increase in patients with cardiovascular diseases. The state-of-the-art treatment for cardiovascular stenosis is an angioplasty in combination with stenting of the affected artery. Stents can be either laser cut out of a tube or an interwoven such as a braided structure. Furthermore, there are two groups of stents regarding their expansion behaviours: balloon expandable and self-expandable. Within this paper, a new approach to braiding stent-like structures out of a novel shape memory polymer fibre will be discussed. Furthermore, the heat treatment of the stent structure will be investigated to improve its characteristics such as radial stiffness.

Key words:

Shape memory polymer, stent, radial resistance force, braiding, heat setting

Introduction

Braiding technology is used to manufacture sutures, artificial ligaments and reinforcement structures for biomedical applications. It is used in particular for stent applications braided from materials such as shape memory alloys (e.g. Nitinol) and shape memory polymers (SMPs) [3] [4]. Current braiding manufacturing technologies are the traditional 2D circular and flat braiding processes, but there are also ambitious activities at the Institut für Textiltechnik to investigate novel 3D braiding processes [7]. Within the project "Mechanisms for the development of proendothelial stents" funded by the "Interdisziplinäre Zentrum für Klinische Forschung" BIOMAT, which is an organisation within the medical faculty of RWTH Aachen University (Germany) to boost interdisciplinary clinical research, novel polymers with shape memory behaviour and improved biocompatibility are investigated regarding the melt spinning of the polymer into monofilaments. In addition, braiding these fibres into stent-like structures and evaluating them in an animal model is carried out. The aim of the project is to develop a stent with good endothelialisation behaviour by using this novel shape memory material. Furthermore, a key aspect in manufacturing braided stents made out of polymer fibres is the decreased radial stiffness and radial resistance force in comparison to metal stents with the same dimensions. Therefore, heat treatment and the merging of the braid intersection points have been examined within the project and will be introduced in this paper.

Materials and methods

SMPs are stimuli-responsive materials, which mean they can change their shapes upon the application of an external stimulus. A change in shape caused by a change in temperature is called a thermally induced shape memory effect. The thermal shape memory effect makes these polymers interesting for medical applications because of their capabilities of expanding at body temperature. The shape memory effect is not related to a specific material property of single polymers; it rather results from a combination of the polymer structure and polymer morphology together with the applied processing and programming technology. Shape memory behaviour can be observed for several polymers that might differ significantly in their chemical compositions. The process of programming and recovering a shape is shown schematically in Figure 1. First, the polymer is conventionally processed to receive its permanent shape. Afterwards, the polymer is deformed and the intended temporary shape is fixed. This process is called programming. The programming process either consists of heating up the sample, deforming, and cooling the sample, or drawing the sample at a low temperature. The permanent shape is then stored, whereas the sample shows a temporary shape. Heating up the SMP above a transition temperature induces the shape memory effect. As a consequence, the recovery of the stored, permanent shape can be observed. Cooling the polymer below the transition temperature leads to the solidification of the material; however, no recovery of the temporary shape can be observed. The effect described is called a one-way shape memory effect. By further programming, including mechanical deformation, the work can return to a temporary shape. However, this new temporary shape does not necessarily match the first temporary shape [6].

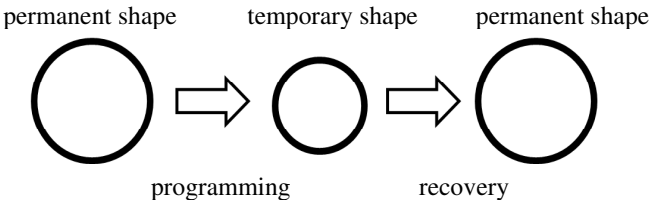

Figure 1. Schematic view of the thermally induced shape memory effect.

For the purpose of developing a braided stent made out of SMP fibres the material Carbothane(r) (Lubrizol Advanced Materials Inc., USA), a polyurethane-based polymer, was used. Carbothane(r) consists of hard and soft domains where hydrogenated methylene diisocyanate represents the hard domains and polycarbonatediol the soft domains. The material was designed for intracorporeal applications and shows good

Table 1. Material parameters of Carbothane(r).

material parameter	unit	value
melt processing	[°C]	185–220
glass transition temperature soft domain	[°C]	–40
glass transition temperature hard domain	[°C]	45–90
durometer range	shore	73A–75D
elasticity	%	250–700

hydrolytic stability as well as good biocompatibility. Table 1 shows the material parameters of Carbothane(r).

In a first step, granules were processed into monofilament fibres. A laboratory piston spinning machine at the Institut für Textiltechnik of RWTH Aachen University was used for this purpose. Owing to the hygroscopic behaviour of Carbothane(r) the material was vacuum dried at 65°C for 4 hours in advance to the spinning process. The used spinneret was a monofilament spinneret with an orifice size of 1 mm. Further process parameters are shown in Table 2.

Table 2. Process parameters of the spin trials.

process parameter	unit	value
melt temperature	[°C]	216
melt pressure	[bar]	65
volumetric flow rate	[cm³/min]	734
take-up speed	[m/min]	25.8

Using these parameters monofilaments with a round cross-section and an average diameter of 200 µm were produced for the braiding trials [1] [2] [5]. The as-spun fibres showed a maximum tensile strength of 14 cN/tex and a maximum elongation of 235%.

A 16 carrier circular braiding machine from August Herzog Maschinenfabrik GmbH & Co KG (Oldenburg, Germany; Figure 2) was used for braid manufacturing. At a constant machine and take-up speed with all bobbin carriers loaded, a braid with an internal diameter of 1.5 mm and a braid angle within the range of 20-30° was produced using a mandrel. Figure 3 shows a braid still fixed to the mandrel, a steel rod with an outer diameter of 1.5 mm.

For the heat treatment of the manufactured SMP braids a heat setting test series with different temperatures and setting periods was used. Temperatures around the glass transition

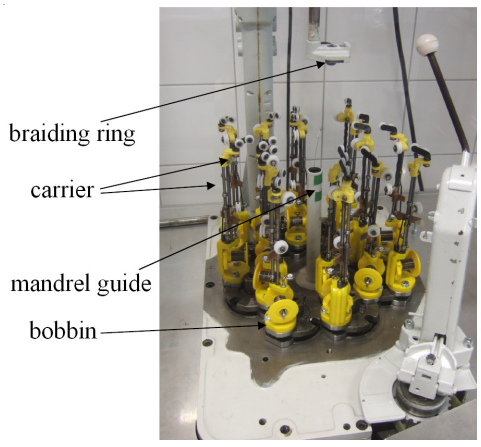

Figure 2. 16 carrier circular braiding machine.

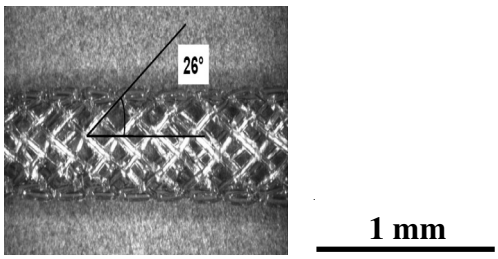

Figure 3. 16 filament SMP braid on a mandrel.

temperature of the material between 70°C and 150°C were investigated. A high temperature oven HT 80.600 (Fresenberger GmbH, Wipperfürth, Germany) was used for the trials (Figure 4). To test the radial stiffness of the manufactured braids and compare them with braids without heat setting crimping tests on a tensile testing machine from Zwick GmbH & Co. KG (Ulm, Germany) were performed.

Figure 4. High temperature oven HT 80.600 (Fresenberger GmbH).

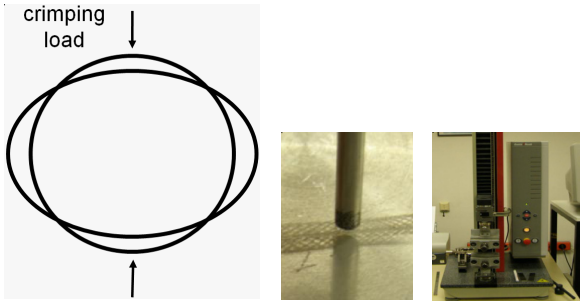

Figure 5. Crimping load (left), crimping test of the SMP braid (middle), tensile testing machine Z 2.5 Zwick GmbH (right).

To test the biocompatibility of the polymer, fibre meshes of the shape memory polyurethane were incubated directly or indirectly (for indirect biocompatibility testing cells were incubated with conditioned medium) with endothelial progenitor cells (EPC) and human umbilical vein endothelial cells (HUVEC). To test the migratory capacity of different cell types (HUVEC & myocytes) in the presence of the polymer a modified Boyden chamber migration assay was used. Unstimulated controls as well as endothelial cell-conditioned media and endothelial progenitor cell-conditioned media were used as a promigratory stimulus in the lower well of the chamber.

Results

Regarding biocompatibility, calcein staining showed a good vitality for EPC attached to the 200 µm monofilaments of the polymer for both direct and indirect testing (Figure 6). In

quantitative vitality tests using XTT proliferation assays (Roche Diagnostics), the material had no significant influence on cell vitality compared with other materials currently in clinical use (Drug Eluting Stent/Vicryl) whether the polymer was incubated with EPC or human smooth muscle cells (HuSMC) (Diagram 1).

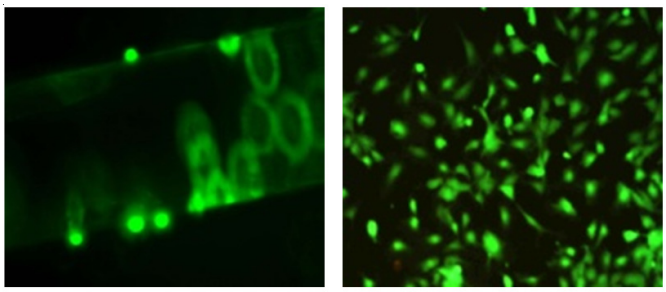

Figure 6. Calcein staining of EPC in the presence of PU (left) and in PU-conditioned media (right).

For the migration capacity of different cell types the results showed no significant influence on the migratory capacity of HUVEC in all groups (Diagram 2, left) but showed a significant reduction in the migratory capacity of myocytes in stimulated groups (Diagram 2, right).

Figure 7 shows microscopic pictures of a selected heat setting test series at different temperatures and a constant time of 10 minutes. It can be seen that at a temperature of 70(C the intersection points are not melted together and at 125(C the intersection points are perfectly merged. A heat setting at 150(C was not useful since the SMP braid was completely melted onto the mandrel. Therefore, no further investigation was possible.

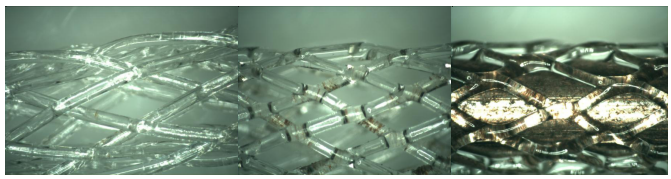

Figure 7. Microscopic pictures of SMP braids (from left to right) heat-treated at 70°C, 125(C and 150°C for 10 minutes.

After heat setting the braid pressure tests were performed. In a first step, the untreated SMP braids were tested and in a second step the radial stiffness of the treated braids was tested using the above described pinching test. Both braid groups were tested with a compression of 1 mm. Diagram 3 and Diagram 4 show the test results of two selected samples. In Diagram 3, it can be seen that the untreated braid shows a maximum radial resistance force of 0.08 N at a compression of 1 mm. In comparison, the treated sample (110°C for 10 min) shows a resistance force more than eight times higher (0.79 N) for the same compression (Diagram 4).

After comparing all heat-treated samples the group treated at 125°C for 10 minutes showed the best radial resistance force. Diagram 5 compares the three braid groups. The first group was untreated, and the second and third groups were treated at 110°C and 125°C respectively for 10 minutes. The radial compression for all groups was 1 mm.

Conclusion

Owing to the good biocompatibility of the material, SMP filaments are generally useful for producing vascular implants such as stents. By using braiding technology and heat treating the braids it has been shown that the radial stiffness of the

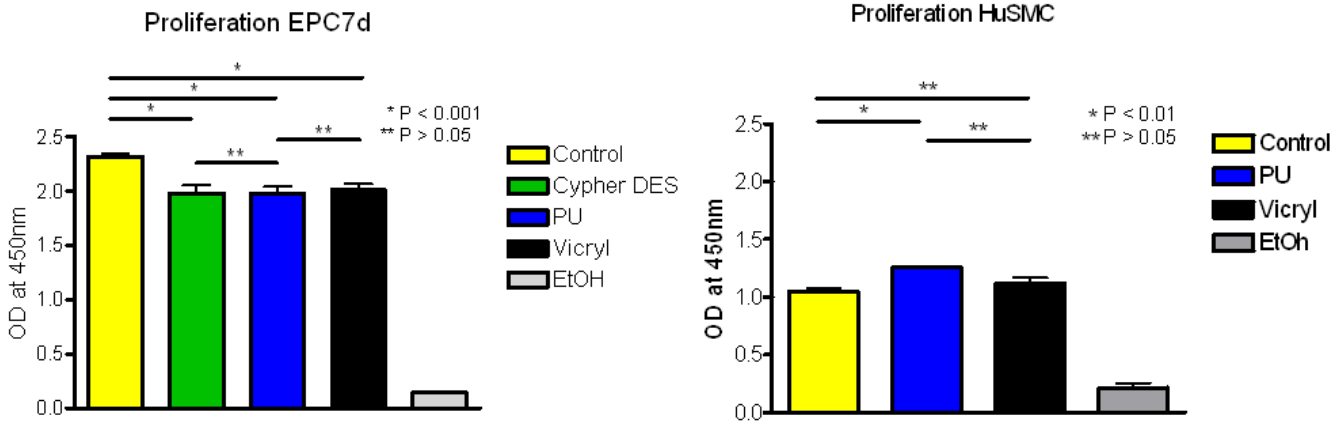

Diagram 1. Proliferation assays with EPC and HuSMC.

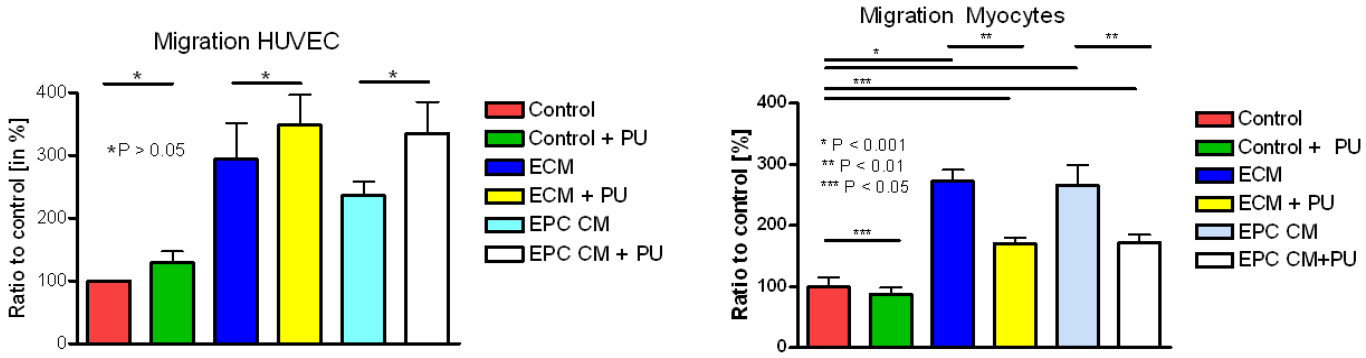

Diagram 2. Boyden chamber assays with HUVEC and myocytes.

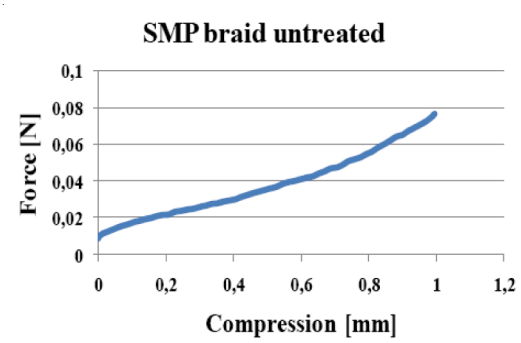

Diagram 3. Pinching test results (compression 1 mm) of an untreated SMP braid.

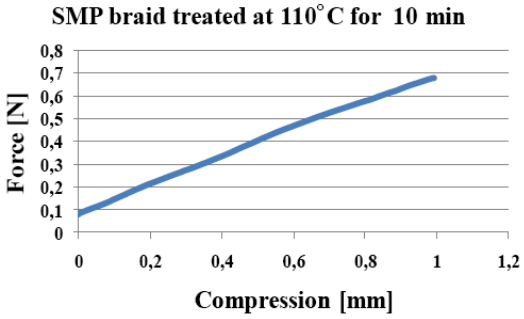

Diagram 4. Pinching test results (compression 1 mm) of a heat-treated SMP braid at 110°C for 10 min.

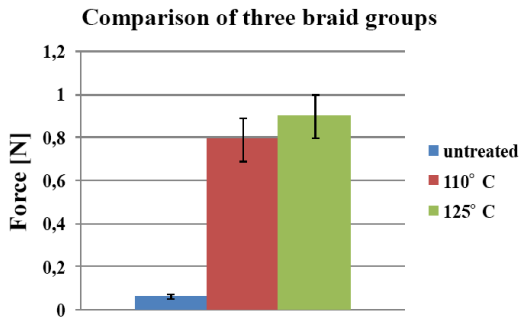

Diagram 5. Comparison of the three different braid groups. Untreated and treated at 110°C and 125°C for 10 minutes with a 1 mm radial compression.

braids was increased. In theory, this radial stiffness should be enough to avoid a stent recoil after implantation. However, a comparison with the market available laser cut or metal wire braided stents still has to be carried out. Taking the results into consideration the SMP braids should be competitive regarding radial stiffness. Furthermore, in an additional step the implantability, re-endothelialisation, and restenosis rate in general in animal studies should be investigated. In particular, the influence of balloon dilatation during implantation was not investigated within the current work. Therefore, a key aspect for a future project is the investigation of the mechanical stability of the connected intersection points of the braid after balloon dilatation.

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References:

1. *Borchert F: Fertigung und Charakterisierung eines textilen Shape-Memory-Polymer-Stents. Institut für Textiltechnik Aachen, RWTH Aachen, Aachen 2007.*
2. *Brüggemann D, Shape Memory Materialien in der Medizintechnik, Bayern Innovativ, Augsburg, 23. Mai 2006.*
3. *Budillon F , Shape Memory Textiles, Shape Memory and superelastic technologies 2004 (SMST 2004), Baden-Baden 3.-7.10.2004, Vortrag-Nr. 171.*
4. *Budillon F, Gries T, Nitinol textiles for medical applications,13th Intern. Techtextil Symposium, Frankfurt, 06.-09.06.2005.*
5. *Houis S, Gries T, Weber C, Kelm M, Blindt R, Shape-memory polymers for vascular stent application, Proceedings BMT 2007 : 41. Jahrestagung der Deutschen Gesellschaft für Biomedizinische Technik (DGBMT) im VDE, Aachen 26.-29.09.2007; Biomedizinische Technik 52 ,Ergänzungsband, 2007.*
6. *Lendlein A, Kelch S, Shape memory polymers, Angewandte Chemie International Edition, 41, 12, pp (2034-2057), 2002.*
7. *Schreiber F, Ko FK, Yang HJ, Amalric E, Gries T, Novel three-dimensional braided textiles for medical and micro composite applications, Küppers, B. (Ed.): Proceedings of the 3rd Aachen-Dresden International Textile Conference, Aachen, November 26-27, 2009. - Aachen : DWI an der RWTH Aachen e.V., 2009.*

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