



HAL
open science

An original architected NiTi silicone rubber structure for biomedical applications

Thierry Rey, Jean-Benoit Le Cam, Grégory Chagnon, Denis Favier, Marie Rebouah, Florence Razan, Eric Robin, P. Didier, Ludek Heller, S. Faure, et al.

► To cite this version:

Thierry Rey, Jean-Benoit Le Cam, Grégory Chagnon, Denis Favier, Marie Rebouah, et al.. An original architected NiTi silicone rubber structure for biomedical applications. *Materials Science and Engineering: C*, 2014, 45, pp.184-190. 10.1016/j.msec.2014.08.062 . hal-03690559

HAL Id: hal-03690559

<https://hal.science/hal-03690559>

Submitted on 8 Jun 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

An original architected NiTi silicone rubber structure for biomedical applications

T. Rey⁽¹⁾, J.-B. Le Cam⁽²⁾, G. Chagnon⁽¹⁾, D. Favier⁽¹⁾, M. Rebouah⁽¹⁾, F. Razan⁽³⁾, E. Robin⁽²⁾, P. Didier⁽³⁾, L. Heller⁽⁴⁾, S. Faure⁽³⁾, K. Janouchova⁽⁴⁾

(1) *Université de Grenoble, CNRS, TIMC-IMAG UMR 5525, Grenoble, France.*

(2) *Université de Rennes 1, Institut de Physique de Rennes, UMR 6251 - CNRS/Université de Rennes 1, Campus de Beaulieu, 35042 Rennes, France.*

(3) *ENS Rennes, SATIE - CNRS 8029, Campus de Ker Lann, 35170 Bruz, France.*

(4) *Institute of Physics ASCR, v.v.i., Na Slovance 2, CZ-182 00 Prague 8, Czech Republic.*

Abstract

This paper deals with composite structures for biomedical applications. For this purpose, an architected tubular structure composed of Nickel Titanium (NiTi) Shape Memory Alloy (SMA) and silicone rubber was fabricated. One of the main interest of such structures is to ensure a good adhesion between its two constitutive materials. A previous study of the authors (Rey *et al.*, 2014) has shown that the adhesion between NiTi and silicone rubber can be improved by an adhesion promoter or plasma treatment. However, adhesion promoters are often not biocompatible. Hence, plasma treatment is in a favour to be used in the present study. Three different gases were tested; air, argon and oxygen. The effects of these treatments on the maximum force required to pull-out a NiTi wire from the silicone rubber matrix were investigated by means of pull-out tests carried out with a self-developed device. Among the three gases, a higher maximum force was obtained for argon gas in the plasma treatment. A tube shaped architected NiTi/silicone rubber structure was then produced using this treatment. The composite was tested by means of a bulge test. Results open a new way of investigations for architected NiTi-silicone structures for biomechanical applications.

Keywords:

Adhesion, interface, composite, NiTi, filled silicone rubber, biomedical applications, architected structure

1. Introduction

Smart materials and structures are widely used to solve biomedical problems. For example, stents are commonly used for several years. Some of the applications using a stent needed a tubular

*Corresponding author: Jean-Benoît Le Cam: jean-benoit.lecam@univ-rennes1.fr, Université de Rennes 1, Institut de Physique de Rennes, UMR 6251 - CNRS/Université de Rennes 1, Campus de Beaulieu, 35042 Rennes, France. Phone number: +33 223 235 741

Email address: jean-benoit.lecam@univ-rennes1.fr (J.-B. Le Cam⁽²⁾)

structure with a small variation in length during radial or bulge solicitations. This shows the interest of such architected NiTi silicone rubber structures for biomedical applications. Some of the studies reported focus on NiTi associated with polymers [1, 2]. To the best knowledge of the authors, the work by Heller *et al.* [3] is the only one dealing with elastomer combined with NiTi. They proposed NiTi-braided elastomer composites for smart structure applications. Each of the two constitutive materials are well known for their typical behavior: NiTi exhibits superelasticity and shape memory behavior, and silicone rubber exhibits hyperelasticity allowing large deformations without permanent set. The use of NiTi was investigated for many applications during the last few years, especially in the medical field [4, 5, 6, 7] due to its biocompatibility [8, 9, 10, 11, 12]. Also, similarly to SMA, elastomers are often considered to make composites [13, 14]. For applications where the composite requires a good mechanical resistance, the efficiency strongly depends on the interface between the NiTi and the polymer matrix. Some investigations to improve their adhesion have already been reported in the literature, highlighting that numerous treatments can change the quality of the interface. Indeed, the adhesion between the two materials can be improved by mechanical [15, 16] or chemical [17] treatments, or by a combination of mechanical, physical and chemical surface treatments [18]. Each treatment presents its own disadvantages: the mechanical treatments are not applicable for every geometries and chemical treatments such as adhesion promoters are often unsuitable for biocompatibility. For these reasons, the use of plasma treatment seems to benefit both of the interface resistance [18, 19] and the interface biocompatibility [20]. It was also used in polymeric materials to improve the efficacy of voice prosthesis [22] or to fulfill the requirements medical in medical applications [23].

The aim of the present study is to fabricate and to characterize the mechanical response of a smart tubular structure, by assembling NiTi wires with silicone rubber whose interface resistance is improved by plasma treatment. Section 2 presents the materials, and the different self-developed devices to test the interface, to produce and to test the composite. Results obtained from the tests performed are given and discussed in section 3. Finally, some concluding remarks close the paper.

2. Experimental setup

2.1. Materials

Commercial pseudoelastic NiTi (50.8 at. % of Ni) SMA wires of 0.5 mm diameter were used for the tests of the interface. The Austenite to Rhombohedral phase (A to R) transformation occurs during cooling at a temperature equal to 0°C and the reverse transformation (R to A) occurs at a temperature equal to 10°C. The Rhombohedral to Martensite (R to M) transformation was not observable by means of DSC, because it occurred at a temperature lower than -90°C, which is the limit of the DSC system used. Thinner NiTi wires with dimensions of 0.1 mm diameter were used to fabricate the composite. Characteristic temperatures were previously identified by DSC [19]. The austenite to rhombohedral (A to R) transformation occurs during cooling at a temperature equal to 30°C and the reverse transformation (R to A) occurs at a temperature equal to 34°C. Like previously, the rhombohedral to martensite (R to M) transformation was not observable on the DSC.

A uniaxial tensile test was performed at room temperature on two NiTi wires. Results are presented in Figure 1. Both wires exhibit large deformations (for a metallic material) with a low residual strain, and a typical superelastic behavior: an (austenitic) elastic part is first observed, followed by a plateau corresponding to a phase transformation (A to M), and a second (martensitic) elastic part. The different values of the plateau during loading and unloading is induced by a

mechanical hysteresis. A biocompatible silicone rubber (Bluestar RTV 4404) was used as polymer matrix. The elaboration process of the silicone rubber is the following: its two components were mixed, this mixture was then degassed, and finally cured for 1 hour at 80°C. The silicone rubber is subjected to cyclic tensile test for four cycles at four increasing maximum strains at room temperature. Results obtained are presented in Figure 1, in terms of the nominal stress (*i.e.* first

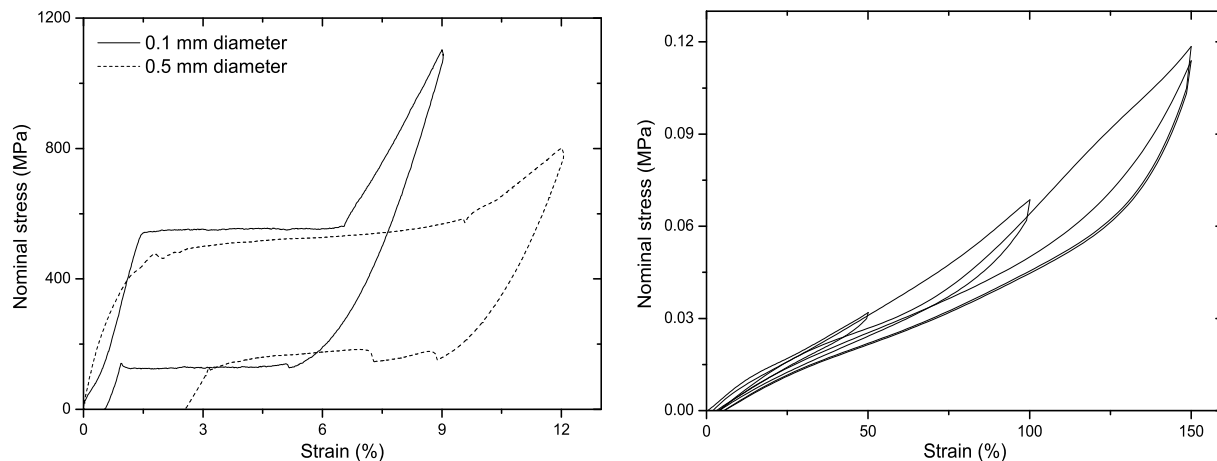


Figure 1: Tensile test on the NiTi wires (on the left) and on a RTV 4404 silicone rubber (on the right).

Piola-Kirchhoff stress, defined as the ratio of the current force by the initial surface) versus strain. Here, several classical phenomena in rubber can be observed. Firstly, rubber undergoes large deformations upon loading with low residual strain after unloading (less than 8% for a maximum strain equal to 150%). Secondly, mechanical hysteresis was observed, *i.e.* difference of stress between loading and unloading. Thirdly, the stress response for subsequent loadings was different. Stress softening or 'Mullins effect' [24] was mainly observed during the first loading.

2.2. Interface characterization

2.2.1. Samples preparation

The adhesion between NiTi and silicone rubber was performed by using a plasma treatment without any chemical substances [18, 19]: a gas under low pressure is subjected to a high frequency oscillating electromagnetic field and the accelerated ions in the gas collide with the gas molecules, ionizing them and forming plasma. The ionized gas particles in the plasma interact with solid surfaces placed in the same environment by removing organic contamination from surfaces and modifying or enhancing the physical and chemical surfaces characteristics [25]. The type of interaction between plasma and surface depends on parameters such as the intrinsic properties sample or gas(es) composition and flux, electrical power, exposure time, pressure [26]... The treatments were carried out with different gases to study their influence on the mechanical response of the NiTi/silicone rubber structure. The plasma treatments using argon or oxygen as working gases were performed using a RIE 300, whereas the plasma treatment with air as working gas was performed using a Harrick Plasma Cleaner. In both cases, the power and exposure time were fixed at 30 W and 720 s respectively. The treatment was performed under vacuum conditions, with operation pressure set equal to 10^{-1} kPa and 2.10^{-2} kPa for the RIE 300 and the Harrick Plasma Cleaner, respectively. Once the wire surface was treated by plasma, it was placed into a self-developed mold, already used in a previous paper of the authors [19]. The mold was then

closed, and the silicone was blended to a curing agent and degassed, before injected into the mold using a medical syringe. Finally, the mold was placed into an oven for 1 hour at 80°C to cure the silicone. The diameter of the cured disk of silicone is 30 mm and the thickness is 5.4 mm.

2.2.2. Pull-out tests

In order to investigate the adhesion between silicone rubber matrix and embedded NiTi wire, pull-out tests were performed. This type of test is classically used in the literature [16, 17, 18, 19, 27] to evaluate the mechanical resistance of the interfaces. For this test, the increase of the adhesion strength is defined by the increase of the maximum required force to pull-out the NiTi wire from the polymer matrix. The pull-out tests were performed using an Instron 5543 testing machine, which load cell capacity is 1 kN. The device is illustrated in a previous paper of the authors [19]. During the test, the sample was kept in the mold to avoid any slipping of the silicone rubber. The mold was mounted in a self-developed device. The wire was placed into the jaw, and was then pulled from the silicone disk in the vertical direction at room temperature and at a displacement rate of 0.6mm/s.

In order to check the interface stability over time, pull out tests were performed at different times after molding, between 0 and 7 days.

2.2.3. Additional analyses

Measurements of the wire deformation were carried out by marks tracking method in order to check that no transformation occurred in the SMA wires during the pull-out tests. Moreover, Scanning Electron Microscopy (SEM) observations were performed with a JEOL JSM 6301F in order to observe surfaces of the pulled-out wires. In order to analyze the effects induced by the plasma treatment, several observations were made before and after the treatment.

Roughness evaluation of a NiTi plate was performed before and after the more efficient plasma treatment. The composition of the NiTi plate is the same than those of the NiTi wires (50.8 at. % of Ni), and its length, width and thickness are 75, 15 and 3 mm, respectively. This analysis was carried out with a surface profiler (Alpha-Step IQ, KLA Tencor). Measurements were performed by means of a diamond tip moving on the specimen surface. For the present measurements, the length, speed and frequency were chosen equal to 500 μm , 20 $\mu\text{m/s}$ and 200 Hz, respectively. The roughness was calculated as the arithmetic average between successive minimum and maximum values of the height (called Ra).

Wettability tests were also carried out on a similar NiTi plate. A liquid droplet was put at the surface of the specimen under study and the diameter and height of this droplet were measured. By this way, the contact angle between the droplet and the specimen can be calculated. The droplet volume is equal to 3 mm³. Two liquids were used: water and diiodomethane. The surface energy was then calculated, using the method proposed in [28].

2.3. Elaboration of the composite

In order to obtain a tubular shaped composite, NiTi wires were knitted and then a shape setting was performed at 450°C (see Figure 2a). The tube obtained was threaded on a metallic tube and fixed to two holding parts in order to avoid any displacement during the injection of the silicone rubber. Then, this tube was treated by plasma for 720 s at 30 W with the working gas giving the best results with the pull-out tests. The treated NiTi tube was then put in a self-developed mold, to be embedded in the polymer matrix, which is injected by the way of a medical syringe. Finally, the mold was placed into an oven at 80°C for 1 hour. The obtained composite is presented in Figure

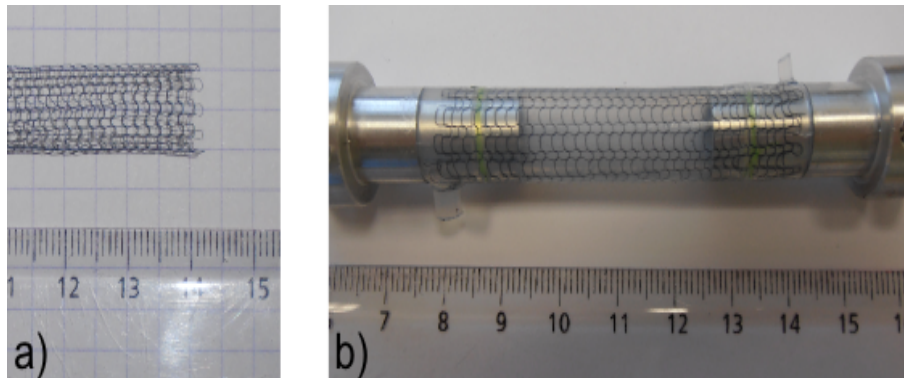


Figure 2: Knitted tube of NiTi (a), tube embedded in a silicone rubber matrix (b).

2b, with the two holding parts at its extremities. Its length, internal and external diameters are 30, 8 and 12 mm, respectively. Several tubes were fabricated in order to check the reproducibility of the process.

2.4. Bulge test

A bulge test was performed by injecting water into the composite. Figure 3 gives an overview of the experimental setup. The composite was suspended by one of the holding parts, and a water

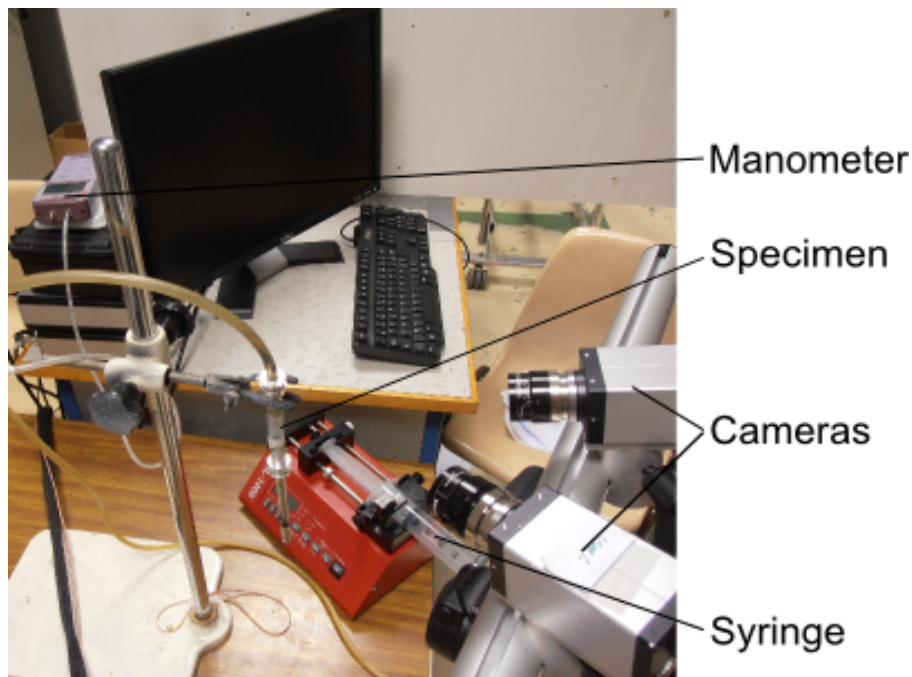


Figure 3: Overview of the bulge test.

injection pipe was connected at this part. The other extremity was closed by a cork. It is worth noting that even though a low amount of force (0.54 N) was imposed (by the weight of the cork and the holding part), the displacements of the inferior part were not blocked. Water was injected

at a constant volume rate by the way of a medical syringe. The pressure in the tube was measured with a manometer.

During the bulge test, the strain field at the composite surface was measured by means of a Stereo Digital Image Correlation (SDIC) system. The CDD sensor of the two cameras used features 1028 X 1028 connected pixels. A speckle pattern was done using a special powder coating on the tube surface for the SDIC, and appropriate lighting has been set up. A marks tracking method was also used to follow the displacement of four crosses at the tube surface and to obtain quantitative values of displacements. Two crosses were marked at the top and bottom of the tube in order to measure length variations, whereas the two others were marked at the center in order to observe the circumference variations.

3. Results and discussion

3.1. Pull-out tests

Results of the pull-out tests are presented in Figure 4 a). Tests were found to be repeatable. Hence, only one curve is plotted for each treatment. The force was found to increase with a plasma

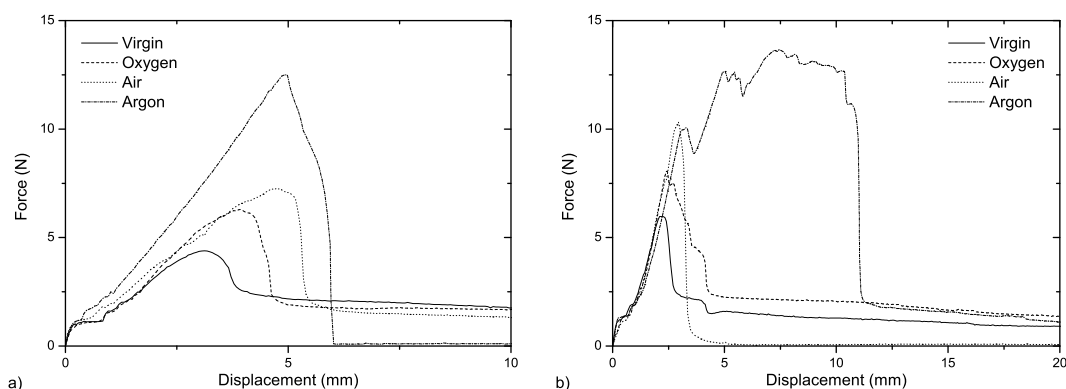


Figure 4: Results of the pull-out tests with different treatments, with a silicone pancake thickness of a) 5.4 mm and b) 2 mm.

treatment regardless the type of gas considered: 33%, 48% and 159% for oxygen, air and argon, respectively.

It is to note that for several applications, thickness of the embedding polymer matrix is not of the same order as the pull-out tests (*i.e.* at least ten times superior than the wire diameter). For this reason, the same tests were carried out with a thickness of the silicone pancake equal to 2 mm. The results obtained are presented in Figure 4 b). This Figure shows that even though the forces reached are different, the trend remains the same as that observed for the classical pull-out tests: the highest maximum forces were obtained for argon, with an increase of maximum force of 158% (14.05 N versus 5.45 N without any treatment). This shows that the efficacy of the treatment and the classification of the treatment do not depend on the thickness of the silicone pancake in the range of thickness tested. Additional pull out tests were carried out using both argon and oxygen (same proportion of each gas), and results showed once again that it is less efficient than using argon only. A comparison with the same tests performed in ref. [19] with another filled silicone rubber (Bluestar RTV 3428) shows that the efficacy of the plasma treatment strongly depends on the nature of the considered polymer. Indeed, in the present study, the treatment with air gas is

less efficient than in [19]. In the present study, the ratio between the maximum forces reached with treated and untreated wires was inferior to 2, while it was superior to 7 in [19]. The results of the wires deformation measurements showed that the local deformations observed on the wires were too low to induce any transformation phenomenon.

Results of the pull-out tests performed several days after molding showed a low increase of the maximum force measured. Even if these results show that the mechanical properties of the interface remained constant at the time scale of several days, additional tests have to be carried out for higher post-molding times, depending on the considered application.

3.2. Post-mortem analysis of the interface zone

SEM observations are presented in Figure 5, for an untreated wire (a), and for wires treated with plasma using oxygen (b), air (c), and argon (d) as working gas. Without any surface treatment, no

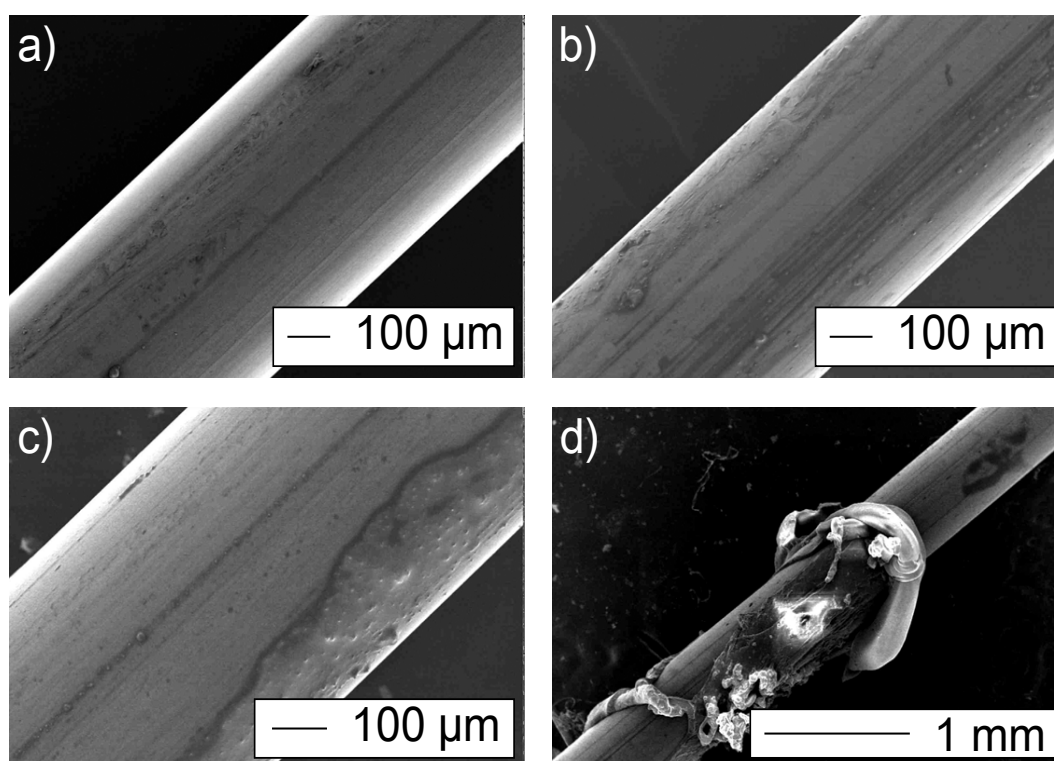


Figure 5: Observation of the pulled-out wires a) without any treatment, and treated by plasma with b) oxygen, c) air and d) argon as working gas.

silicone rubber was observed on the surface of the pulled-out wire, whereas a few parts of silicone were observed for a wire treated with oxygen and air. As shown in Figure 5d), the surface treated with argon gas exhibited large silicone rubber patches which indicates that significant cohesive failures took place in the material before any adhesive failure. This confirms the best efficacy of the plasma treatment with argon. For each condition, no modifications on the surface of the wire were observed for areas without silicone. Results obtained for the roughness analyses showed that the roughness remained constant before and after the argon gas plasma treatment (R_a equal to $0.706 \mu\text{m}$ before and $0.695 \mu\text{m}$ after the treatment). Hence, the plasma treatment does not affect the surface of the NiTi wire, confirming the SEM observations on the pulled-out wire.

Results of the wettability analyzes show that the wettability is increased by plasma treatment with argon gas. Indeed, the contact angle measured for water and diiodomethane were equal to 56° and 37° against 17° and 39° before treatment respectively, giving an increase of the surface energy from 50 mJ/m^2 to 70 mJ/m^2 .

3.3. Bulge tests

As mentioned earlier, the composite was bulged by water injection. Several cycles were carried out in order to investigate the possible irreversibilities in the mechanical response. Figure 6 presents the pressure variation during 10 cycles with an injected water volume of 5 cm^3 . The measurements

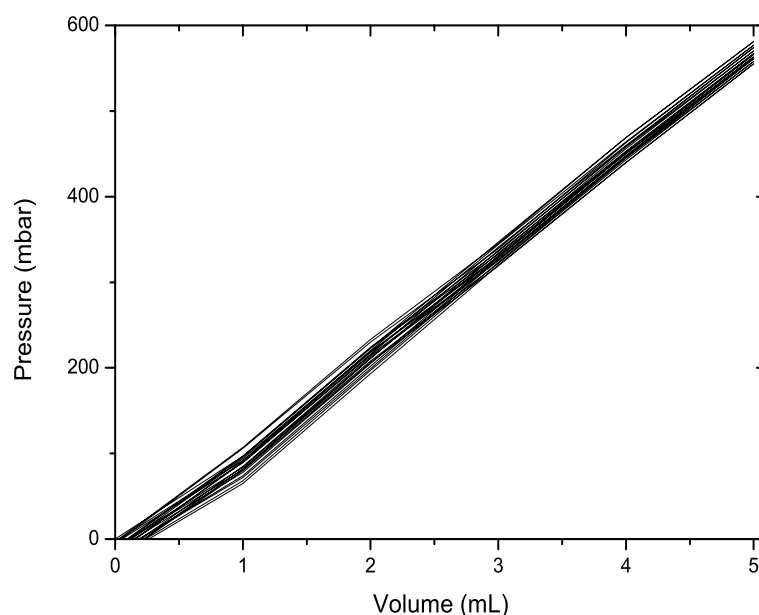


Figure 6: Bulge test of the architected composite.

were not performed during the first cycle, as it is a cycle of setting up of the system. Thus the cycles presented in the figure are from the 2^{nd} to the 11^{th} . It is observed on this curve that a small amount of permanent set existed between each cycle. Therefore, the mechanical response was considered to be similar throughout the test.

Variation of the tube dimensions were measured during the test by means of marks tracking method. During the test, the tube was kept in a circular shape. So, an increase of the distance between the two points in the radial direction corresponds to an increase of the diameter. It was observed that the diameter of the center of the composite increased during the injection of water. At the same time, its length decreased during injection. It should be noted that the composite rotated slightly during the test. These three effects were induced due to the response of the knitted NiTi tube: the mesh get tighten itself, inducing a length reduction because stitches are closer, and rotation because the knitting was carried out by a helical method.

In order to analyze the displacements and deformations at the tube surface, SDIC analyses were also performed during the test. The error on the strain measurements was equal to 0.1%. Figure 7 presents the distribution of the stretches in the diameter and length directions (λ_1 and λ_2 respectively), at a pressure slightly lower than 60 kPa. The stereo-correlation results confirmed

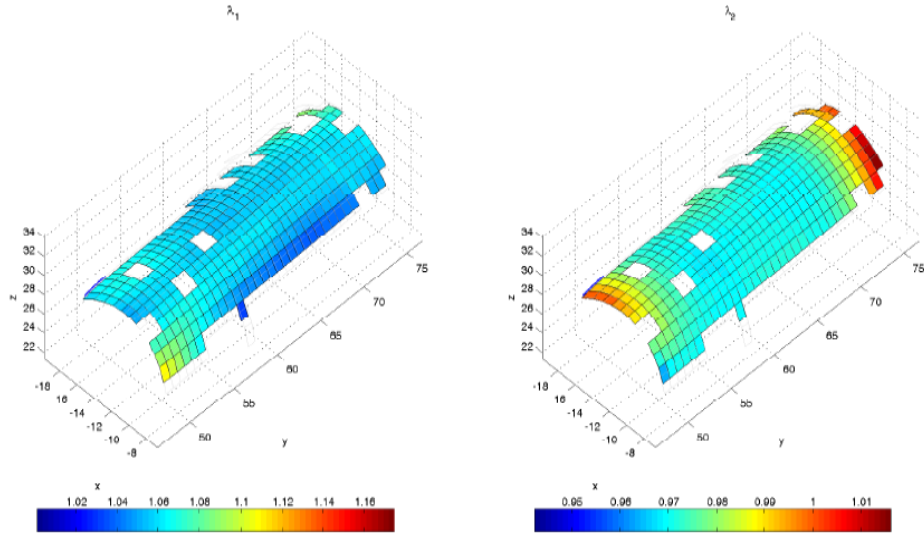


Figure 7: Estimation of the stretches by means of stereo-correlation measurements in the diameter (1) and length (2) directions.

that the composite diameter increased whereas the length decreased. Here, measurements made close to the holding parts are not taken into account in the analysis, as the 3D reconstruction was distorted due to the clipping of the tube. It can be observed that for a pressure slightly lower than 60 kPa, the strain reached in the diameter direction is equal to 7% in tension whereas it is equal to 3% in compression in the length direction.

A tube of silicone rubber was bulged by the same way in order to analyze the influence of the tubular NiTi structure. Figure 8 presents the results of the bulge tests for a silicone rubber tube and a NiTi silicone rubber tube. It can be observed in Fig. 8 a) that the addition of the

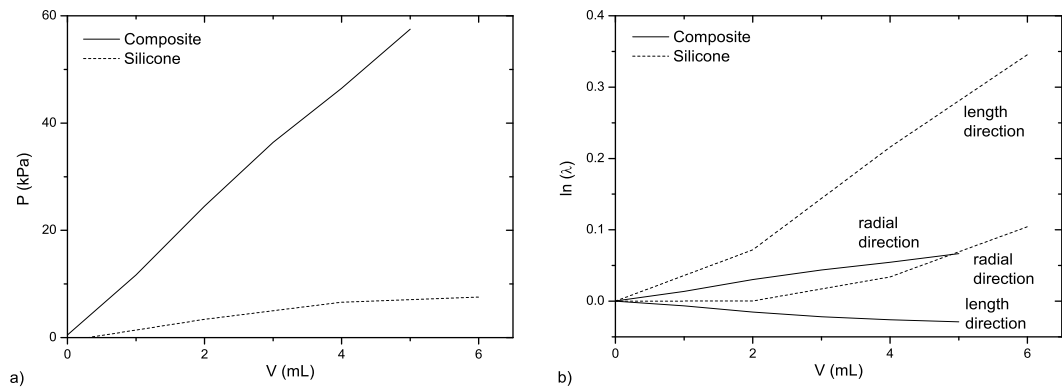


Figure 8: Comparison between the bulge of a silicone rubber tube and a NiTi silicone rubber composite tube.

knitted NiTi tube led to a significant increase of stiffness of the structure. Indeed, the measured pressure in NiTi silicone rubber tube was very higher than for silicone rubber tube (for example, for a volume of 5 mL, the pressure in the composite tube was equal to 57 kPa instead of 6.5 kPa for silicone rubber, *i.e.* almost 9 times higher). Fig. 8 b) shows that the stretch measured in the longitudinal direction was more important than the one in the radial direction for silicone rubber

only, and positive logarithmic stretches were observed in the two directions. For the composite, the logarithmic stretch in the longitudinal direction was negative, and less important than the stretch in the radial direction.

3.4. Discussion

Results highlighted that the composite tube behavior was very different from a tube of silicone rubber. Indeed, as previously observed, the tube of silicone rubber increases its length and diameter during a bulge test. The increase in length is higher than the increase in diameter. It reaches 35% of the initial length, which is not compatible with biomedical applications. When a knitted NiTi structure is used, the length slightly decreased instead of increasing steeply. Moreover, in this case, the length of contraction is lower than the diameter expansion (7%). This is a major advantage offered by such NiTi silicone rubber composite. Several other advantages can also be pointed out.

Firstly, its mechanical behavior can be easily modified. Indeed, it is mainly determined by the mechanical response of the knitted NiTi, whose mechanical behavior can be altered through heat treatments. Secondly, the mechanical response of the knitted tube can be modified by changing the mesh size or by using two wires with different mechanical behaviors before the shape setting step. For instance, to induce a type of anisotropy similar to that observed in soft tissues. Thirdly, the behavior of a NiTi based composite can be driven by several ways: it is well known to react with mechanical, thermal and electrical solicitations. For thermal and electrical solicitations, the silicone rubber isolates the NiTi from the tissues. Finally, no detectable mechanical response changes were observed during cyclic loadings. This offers many possibilities and such a composite should strongly be considered for applications, typically for applications like artificial vessels or stents.

4. Conclusion

In this paper, a composite structure has been proposed to meet the specific needs in the biomedical field. The composite structure was fabricated by associating a knitted NiTi with a silicone rubber. The interface resistance between both materials was improved by an optimized plasma treatment without any adhesion promoter. A tubular shaped composite structure was fabricated using a self-developed device and submitting it to cyclic internal pressure during a bulge test. Results have shown that under pressure, the strain level is low. The tube contracts in the longitudinal direction and stretches in the radial direction. Consequently, this particular composite structure provides promising aspects for biomedical applications, especially to fabricate artificial vessels or stents.

Acknowledgement

This work has been supported by the French National Research Agency Program n2010BLAN90201 ANiM (Architected NiTi Materials). The authors acknowledge Mei Sze Loo for fruitful discussions and valuable suggestions.

References

- [1] K. Neuking, A. Abu-Zarifa, S. Youcheu-Kemtchou, G. Eggeler, Polymer/NiTi-composites: Fundamental aspects, processing and properties, *Adv. Eng. Mater.* 7 (2005) 1014–1023.
- [2] C. J. de Araújo, L. F. A. Rodrigues, J. F. Coutinho Neto, R. P. B. Reis, Fabrication and static characterization of carbon-fiber-reinforced polymers with embedded NiTi shape memory wire actuators, *Smart Mater. Struct.* 17 (2008) 065004.
- [3] L. Heller, D. Vokoun, P. Šittner, H. Finckh, 3D flexible NiTi-braided elastomer composites for smart structure applications, *Smart Mater. Struct.* 21 (2012) 045016.
- [4] T. Duerig, A. Pelton, D. Stöckel, An overview of nitinol medical applications, *Mater. Sci. Eng. A* 273 (1999) 149–160.
- [5] N. Morgan, Medical shape memory alloy applications-the market and its products, *Mater. Sci. Eng. A* 378 (2004) 16–23.
- [6] L. Petrini, F. Migliavacca, Biomedical applications of shape memory alloys, *J. Metal.* 2011 (2011) ID 501483.
- [7] A. Nespoli, V. Dallolio, F. Stortiero, S. Besseghini, F. Passaretti, E. Villa, Design and thermo-mechanical analysis of a new NiTi shape memory alloy fixing clip, *Mat. Sci. Eng. C* 37 (2014) 171–176.
- [8] M. Berger-Gorbet, B. Broxup, C. Rivard, L. Yahia, Biocompatibility testing of NiTi screws using immunohistochemistry on sections containing metallic implants, *J. Biomed. Mater. Res.* 32 (1996) 243–248.
- [9] M. Es-Souni, M. Es-Souni, H. Fischer-Brandies, Assessing the biocompatibility of NiTi shape memory alloys used for medical applications, *Anal. Bioanal. Chem.* 381 (2005) 557–567.
- [10] J. Khalil-Allafi, B. Amin-Ahmadi, M. Zare, Biocompatibility and corrosion behavior of the shape memory NiTi alloy in the physiological environments simulated with body fluids for medical applications, *Mat. Sci. Eng. C* 30 (2010) 1112–1117.
- [11] J. M. Jani, M. Leary, A. Subic, M. A. Gibson, A review of shape memory alloy research, applications and opportunities, *Mater. Design* (2013) <http://dx.doi.org/10.1016/j.matdes.2013.11.084>.
- [12] A. Bansiddhi, T. Sargeant, S. Stupp, D. Dunand, Porous NiTi for bone implants, *Acta Biomater.* 4 (2008) 773–782.
- [13] T. Oppenheim, T. Knowles, S. Lacour, M. Welland, Fabrication and characterisation of protein fibril-elastomer composites, *Acta Biomater.* 6 (2010) 1337–1341.
- [14] W. Thein-Han, J. Shah, R. Misra, Superior in vitro biological response and mechanical properties of an implantable nanostructured biomaterial: Nanohydroxyapatite-silicone rubber composite, *Acta Biomater.* 5 (2009) 2668–2679.
- [15] K. Jonnalagadda, G. Kline, N. Sottos, Local displacements and load transfer in shape memory alloy composites, *Exp. Mech.* 37 (1997) 78–86.
- [16] K. Lau, W. Tam, W. Meng, L. Zhou, Morphological study on twisted NiTi wires for smart composite systems, *Mater. Lett.* 57 (2002) 364–368.
- [17] N. Smith, G. Antoun, A. Ellis, W. Crone, Improved adhesion between nickel–titanium shape memory alloy and a polymer matrix via silane coupling agents, *Compos. Part A-Appl. S.* 35 (2004) 1307–1312.
- [18] K. Neuking, A. Abu-Zarifa, G. Eggeler, Surface engineering of shape memory alloy/polymer-composites: Improvement of the adhesion between polymers and pseudoelastic shape memory alloys, *Mater. Sci. Eng., A* 481 (2008) 606–611.
- [19] T. Rey, F. Razan, E. Robin, S. Faure, J.-B. Le Cam, G. Chagnon, A. Girard, D. Favier, Mechanical characterization and comparison of different NiTi/silicone rubber interfaces, *Int. J. Adhes. Adhes.* 48 (2013) 67–74.
- [20] J. Sui, Z. Gao, W. Cai, Z. Zhang, DLC films fabricated by plasma immersion ion implantation and deposition on the NiTi alloys for improving their corrosion resistance and biocompatibility, *Mater. Sci. Eng., A* 454 (2007) 472–476.
- [21] Z. Huan, L. Fratila-Apachitei, I. Apachitei, J. Duszczek, Porous NiTi surfaces for biomedical applications, *Appl. Surf. Sci.* 258 (2012) 5244–5249.
- [22] E. Everaert, B. Van de Belt-Gritter, H. Van der Mei, H. Busscher, G. Verkerke, F. Dijk, In vitro and in vivo microbial adhesion and growth on argon plasma-treated silicone rubber voice prostheses, *J. Mater. Sci.-Mater. M.* 9 (1998) 147–157.
- [23] C. Oehr, Plasma surface modification of polymers for biomedical use, *Nucl. Instrum. Meth. B* 208 (2003) 40–47.
- [24] L. Mullins, Effect of stretching on the properties of rubber, *Rubb. Chem. Technol.* 21 (1948) 281–300.
- [25] H. Winters, J. Coburn, Surface science aspects of etching reactions., *Surf. Sci. Rep.* 14 (1992) 161–269.
- [26] S. Rossnagel, J. Cuomo, W. Westwood, Handbook of plasma processing technology : fundamentals, etching, deposition, and surface interactions., Park Ridge, N.J., 1990.

- [27] S. Sadrnezhaad, N. Nemati, R. Bagheri, Improved adhesion of NiTi wire to silicone matrix for smart composite medical applications, *Mater. Design* 30 (9) (2009) 3667–3672.
- [28] D. Owens, R. Wendt, Estimation of the surface free energy of polymers, *J. Appl. Polym. Sci.* 13 (1969) 1741–1747.