International Journal of Adhesion & Adhesives 48 (2014) 67–74

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Mechanical characterization and comparison of different NiTi/silicone rubber interfaces

T. Rey [a], F. Razan [c], E. Robin [b], S. Faure [c], J.-B. Le Cam [b,*], G. Chagnon [a], A. Girard [d], D. Favier [a]

[a] UJF-Grenoble 1, CNRS, TIMC-IMAG UMR 5525, Grenoble, France
[b] Université de Rennes 1, L.A.R.M.A.U.R. - CNRS 6274, Campus de Beaulieu, Bât. 10B, 35042 Rennes Cedex, France
[c] ENS Cachan Bretagne, Campus de Ker Lann, 35170 Bruz, France
[d] IETR, Campus de Beaulieu, 35042 Rennes Cedex, France

ARTICLE INFO

Article history:
Accepted 15 July 2013
Available online 2 October 2013

Keywords:
NiTi
Silicone rubber
Interface
Adhesion
Composite
Plasma
Primer

ABSTRACT

This paper investigates the effects of different surface treatments on the mechanical resistance of interface between wires of NiTi shape memory alloy and silicone rubber. Three different treatments were used; primer, plasma and combination of both. The wires deoxidation effects have also been studied. In order to characterize the interface properties in such composite material, pull-out tests were carried out by means of a home-made device. This test allows us to evaluate the mechanical resistance of the interface in terms of the maximum force reached during the test. First, results show that the debonding force is not higher after the wires deoxidation. This preparation is therefore not necessary. Second, using a primer PM820 and plasma separately leads to a significant improvment of the mechanical resistance. Third, the combination of these treatments (primer followed by plasma) and a longer time of exposure to the plasma alone get the debonding force higher. Consequently, NiTi/silicone rubber interface improved only by means of plasma offers a new way to obtain biocompatible interfaces in such composite material.

1. Introduction

Shape Memory Alloys (SMA) and more specifically Nickel–Titanium (NiTi) are increasingly used in many applications due to their typical behavior, *i.e.* their superelasticity and their shape memory behavior. This type of materials undergoes relatively large deformations of about 10% without exhibiting any plasticity in the pseudoelastic domain [1]. It allows large deformations too in its shape memory form, but a permanent deformation is observed. In the latter case, it can return to its initial shape by heating. The properties of shape memory alloys can be activated either by mechanical or thermal loadings that explain their large use, especially in the biomedical field and in the aerospace. New categories of innovative materials can be developed by combining the intrinsic properties of these SMA with purposely engineered topologies [2] or with intrinsic properties of other materials such as polymers [3] or elastomers [4]. To realize these unique structures, innovative materials processing techniques are applied such as electrical resistance welding to link NiTi tubes [5], or embedding of NiTi in a polymer matrix [6].

The efficiency of these composites strongly depends on the adhesion between the NiTi and the polymer matrix. Some investigations to improve this adhesion have already been reported in the literature. They highlight that numerous treatments can change the quality of the interface. Neuking et al. [7] observed that the adhesion between NiTi wires and a thermoplastic polymer can be improved by a combination of mechanical, physical and chemical surface treatments. Smith et al. [8] showed the efficiency of silane coupling agents to improve the interface between NiTi wires and a PMMA matrix. For NiTi/epoxy composites, Jonnalagadda et al. [9] showed that the debonding force can be significantly increased by sandblasting the NiTi wires. This treatment is efficient but not suitable for all applications, typically for very little NiTi specimens, due to the sand particles size. In [10], NiTi wires were twisted and next embedded in an epoxy matrix. The geometrical changes and the increase of roughness (by mechanical breaking of the surface oxide film of the wire due to the twisting process) increase the bonding strength. Once again, this treatment seems to be efficient, but it is only possible for the use of wires, and an unrecoverable strain can appear on the wires in the case of a too great number of turns.

Even though numerous studies were carried out on NiTi/polymer interfaces, the interface between NiTi and a silicone rubber has rarely been investigated. Nevertheless, a main result has already been obtained: the interface is improved by acid etching and oxidizing the NiTi wires [11]. This NiTi/silicone rubber association is often used, as an example for smart structure applications [12] or for actuators [13,14]. The interface between

* Corresponding author. Tel.: +33 223 235 741; fax: 33 223 236 111.
E-mail address: jean-benoit.lecam@univ-rennes1.fr (J.-B. Le Cam).

0143-7496/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ijadhadh.2013.09.028

silicone rubber and other materials has also been studied. In [15], a primer was used to improve the adhesion between polyurethane and silicone. In [16], an argon–oxygen plasma was used to improve adhesion between collagen and silicone.

This paper aims therefore at investigating the interface NiTi/silicone rubber. The materials and devices are presented in Section 2. In Section 3, results obtained from different treatments on the NiTi wires are presented. More precisely, the effects of deoxidation of NiTi wires and the differences between interfaces made with adhesion promoter and plasma treatment are discussed related to the maximum force reached during mechanical tests. Finally, concluding remarks close the paper.

2. Materials and methods

2.1. Materials

Wires of commercial pseudoelastic NiTi (with a Ni content of 50.8 at%) shape memory alloy were used. The diameter of the wires is 0.5 mm. The characteristic temperatures of this material were identified by means of a DSC (Differential Scanning Calorimetry), using a TA Q200 differential scanning calorimeter. It consists in a cooling between 120 °C and −90 °C followed by a heating between −90 °C and 120 °C. Cooling and heating rates were set at 10 °C per minute. A specimen of 20 mg weight was used. The results of the DSC analysis are presented in Fig. 1. Two peaks are observed. They correspond to the austenite (A) to rhombohedral (R) phase transformation (A to R) during the cooling and the reverse transformation (R to A) during the heating. These peaks are interpreted as the A to R and reverse transformations and not as austenite to martensite (M) phase (and reverse) transformation because the small difference between the two peaks ($T_{R-A}-T_{A-R}\approx 10$ °C) and the low latent heats (about 3 J/g) are representative of the A to R and reverse transformations [17]. The R to M phase transformation (and its reverse) is not visible in the DSC, meaning that the temperature of the R to M transformation is lower than −90 °C.

A curve of a classical load–unload tensile test of the NiTi at room temperature is presented in Fig. 2. This curve presents a first elastic part, followed by a plateau corresponding to a phase transformation (A to M), and an elastic response of martensite phase. A hysteresis loop is observed, as the level of the plateau is different during load and unload.

The polymer matrix considered here is a filled silicone rubber (Bluestar RTV 3428). The mechanical and thermal properties of this material were previously investigated in [18,19]. Its

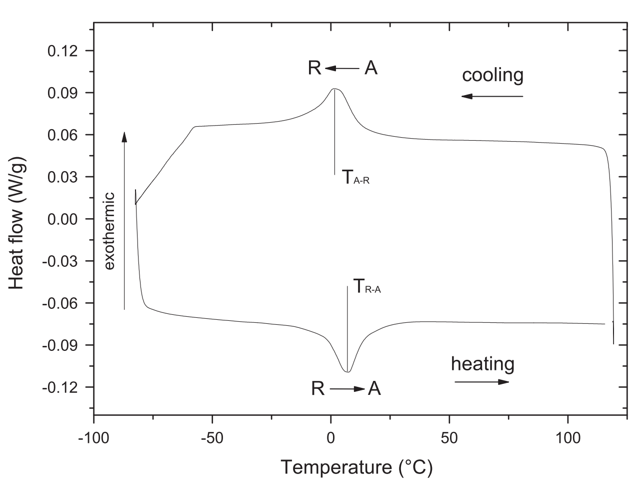

Fig. 1. DSC analysis of the NiTi wire.

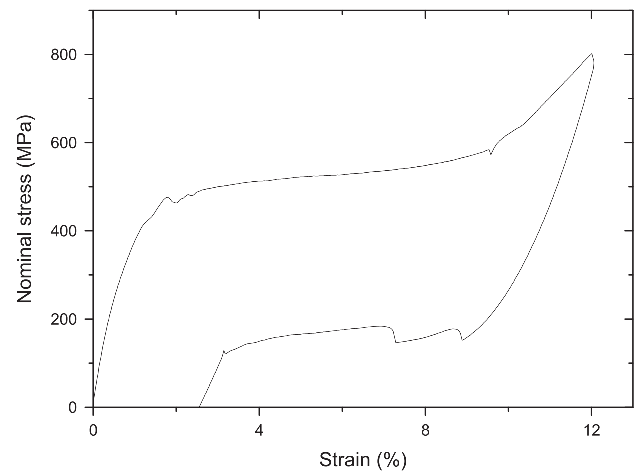

Fig. 2. Load–unload tensile test on a NiTi wire at room temperature.

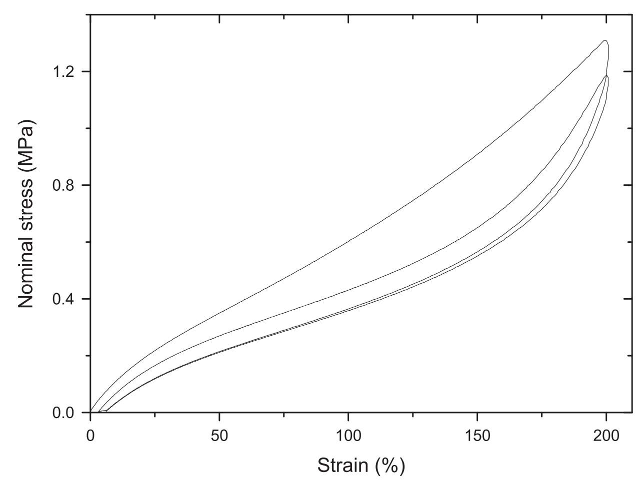

Fig. 3. Load–unload tensile test (two cycles) on a RTV 3428 silicone rubber at room temperature.

crystallization and melting temperatures were identified by a DSC (cooling and heating rates: 2 °C per minute) at −66 °C and −41 °C respectively, and the glass transition temperature is lower than −90 °C [19]. The material exhibits a hyperelastic behavior and undergoes high strain levels. Moreover, numerous phenomena take place during its deformation. Results of a tensile test with two load–unload cycles are presented in Fig. 3. A stress softening is observed between first and second loads, corresponding to the Mullins effect [20]. Moreover, a difference between the mechanical response during loads and unloads is observed, it is the mechanical hysteresis. Finally, a little residual elongation is observed after unloading.

A PM820 primer from Bluestar Silicone is used in some cases as an adhesion promoter. It is recommended by Bluestar Silicone to improve the adhesion between a metallic surface and an elastomer.

2.2. Samples preparation

A home-made mold was designed to ensure the NiTi wire to be located in the center of the silicone rubber pancake. Moreover, the mold enables to control the thickness of the silicone specimen, as illustrated in Fig. 4a. The dimensions of the pancake composite are given by the schematic diagram in Fig. 4b. Once the treated wire was put in the mold, the silicone, which was previously blended with its curing agent and degassed to remove air bubbles, was