DEVELOPMENT OF AN ACTIVE EPOXY COMPOSITE WITH EMBEDDED SHAPE MEMORY ALLOY WIRES

Artur S. C. Leal, e-mail: arturcleal@yahoo.com.br
Alysson D. de Oliveira, e-mail: allyssondaniel@yahoo.com.br
Wanderley Ferreira de Amorim Jr, e-mail: engenheiromec@yahoo.com.br
Carlos José de Araújo, e-mail: carlos@dem.ufcg.edu.br
Zoroastro Torres Vilar, e-mail: zoro.ufcg@gmail.com
André Fellipe Cavalcante Silva, e-mail: af_andre.fellipe@hotmail.com

Universidade Federal de Campina Grande (UFCG)
Rua Aprígio Veloso, 882 – Caixa Postal 10069
Bairro Universitário – CEP: 58429-900
Campina Grande – PB, Brazil

Abstract: In this work, active composites of epoxy resin containing Ni-Ti Shape Memory Alloy (SMA) thin wires were fabricated to evaluate its thermomechanical behavior in the range of phase transformation of SMA during heating. The epoxy resin system employed was prepared using bifunctional diglycidyl ether of bisphenol A (DGEBA) and crosslinking agent triethylenetetramine (TETA). The evaluated ratio DGEBA/TETA was 100:20 and the SMA volumetric fraction of Ni-Ti wires were 1.9 % and 3.8 %. The phase transformation of the Ni-Ti SMA wires were determined by Differential Scanning Calorimetry (DSC) and the specimens of the epoxy – SMA active composites were characterized by Dynamic Mechanical Analysis (DMA). According to the DMA results it was evidenced a significant increase of storage modulus in the active composite during heating in the range of the phase transformation of Ni-Ti SMA wires when the volumetric fraction is of the order of 3.8 %. Moreover, when small amounts of SMA were incorporated, as for example, 1.9 %vol., no effect was observed because the SMA content was not enough for the phase transformation of the Ni-Ti wires act on the epoxy matrix. Finally, these preliminary results have confirmed that development of smart composites may be expected by using embedded SMA wires in polimeric matrix.

Keywords: Shape memory alloys, Active composites, Dynamic mechanical analysis, Storage modulus.

1. INTRODUCTION

Active composites can be prepared with the incorporation of pure smart materials in a polymeric matrix. The attainment of this class of materials allows a set of new opportunities and technological innovation, since the need for more resistant materials, lighter, versatile and above all with some degree of functionality controlled by environmental parameters such as temperature and electrical current can become an industrial reality in near future.

The Shape Memory Alloys (SMA) are metallic materials that demonstrate the ability to recover an "apparently plastic" deformation or to develop considerable forces when is limited to recovering its original shape after the imposition of an external stimulus, as temperature or electric power, inducing the phase transformation of the material. This phenomenon occurs due to a solid-state reversible thermoelastic martensitic phase transformation and is called Shape Memory Effect (SME). At higher temperatures there is the austenite phase, whereas by cooling the material, the martensite phase appears gradually (Otsuka and Wayman, 1998).

The SMA is used in various applications such as actuators and damping devices to a variety of areas, such as biomedicine, aerospace, mechatronics and electronics, but several studies reported in the literature are being directed to the use of SMA embedded in polymeric matrix, mainly epoxy, forming smart composites, as they are known (Lau *et al.*,2002 ; Michaud, 2004; Ni *et al.*, 2007; de Araújo *et al.*, 2008; Vilar *et al.*, 2010; Raghavan *et al.*,2010).

According to De Araújo *et al.* (2008), the introduction of SMA thin wires (0.075mm <diameter <0.6mm) into a structure or polymer matrix offers the advantage of incorporating low-mass at the system could greatly increase its rigidity or cause a significant change of its shape. Therefore, the system can no longer be completely passive and gain an active state as a function of temperature or electric current in the case of Joule effect heating.

In the present paper, a smart composite of epoxy resin with Ni-Ti SMA continuous wires were fabricated. The main objective is to develop active composites with high properties of recovering stiffness (storage modulus) by the phase transformation of SMA during heating.

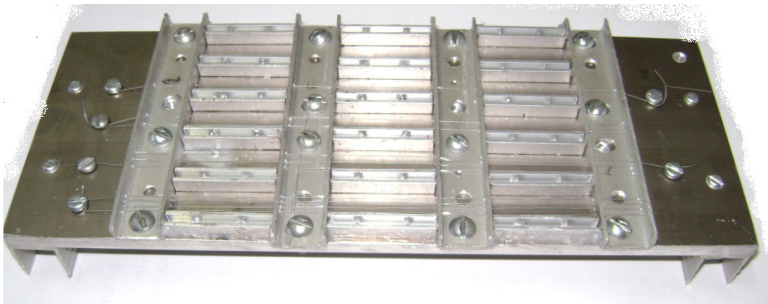
2. EXPERIMENTAL PROCEDURES

2.1. Materials

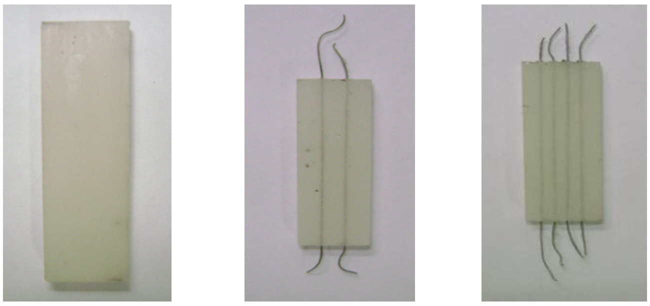
The SMA used in the present study were Ni-Ti binary SMA wire of 0.29 mm in diameter, named alloy M, obtained from Memory-Metalle Inc. (Germany). Firstly the as-received Ni-Ti wire was annealed at 450 C for 20 min, followed by cooling in air at room temperature. This heat treatment releases the reversible martensitic transformation responsible for the emergence of the SME phenomenon. The phase transformation temperatures of the Ni-Ti SMA wires were determined by DSC using a cooling/heating rate of 5 ºC/min. The polymer used as a matrix for the composite was diglycidyl ether of biphenyl A (DGEBA) epoxy resin, and the hardening agent was triethylenetetramine (TETA) in proportion of 100:20. Both, the epoxy resin and the curing agent are produced by Silaex® Química Ltda (São Paulo, Brazil).

2.2. Specimen fabrication

For the fabrication of the active composite a specific quantity (28 g) of DGEBA and 5.6 g of hardener was heated at 40 °C for 20 minutes. Once, curing agent was added and the mixture was stirred for 5 min before being cast in a metallic mold with aligned heat-treated Ni-Ti SMA wires. Figure 1 show the previously manufactured metallic mold (Fig. 1a) with rectangular cavities (30.0x12.7x3.2 mm) corresponding to the shape of the test specimens for DMA analysis (Fig. 1b). The contents in volume of SMA wires were 1.9% and 3.8 %, respectively. The epoxy composites were then cured for 72 h at 25 ºC and post-cured at 110 ºC for 3 h (Su *et al.*, 2002).



(a)



(b)

Figure 1. Metallic mold (a) and the manufactured active epoxy-SMA composite specimens (b).

2.3. Experimental tests

In order to study the thermomechanical properties of the epoxy-SMA composites, all samples were examined by DMA analysis. Dynamic mechanical properties of the composites were measured with a TA Q800 DMA analyzer in a single cantilever mode with a fixed frequency of 1 Hz and 15 μm of tip deflection oscillation amplitude. A temperature ramp from 30 to 150 °C at 2 °C/min was used for all tests. The glass transition temperature (T_g) was determined from the peak of the loss factor (tan δ) curve.

3. RESULTS AND DISCUSSION

In general, four temperatures related to phase transformation of SMA are very important to describe the thermomechanical behavior of the Ni-Ti wire: A_s, A_f, M_f, and M_s which are the start and finish transformation temperatures from martensite to austenite and from austenite to martensite phase, respectively. Figure 2 shows the heat flow DSC curves of the Ni-Ti SMA wires heat-treated at 450º C for 20 min. The transformation temperatures of the

SMA wire determined in Fig. 2 are summarized in Tab. 1. As is well known from the literature (Otsuka and Wayman, 1998), it was observed that the Ni-Ti wire actuator transforms in two-step during cooling, from austenite to the R-phase (R_s = 59.2 °C and R_f = 31.6 oC) and then to martensite (M_s = 38.6 °C and M_f = 8.0 °C). Thermal activation by heating occurs in a single step, starting at A_s = 53.8 °C and is completed at about A_f = 61.3 °C. Then, complete activation of the Ni-Ti wires by heating occurs for temperatures higher than 62 °C.

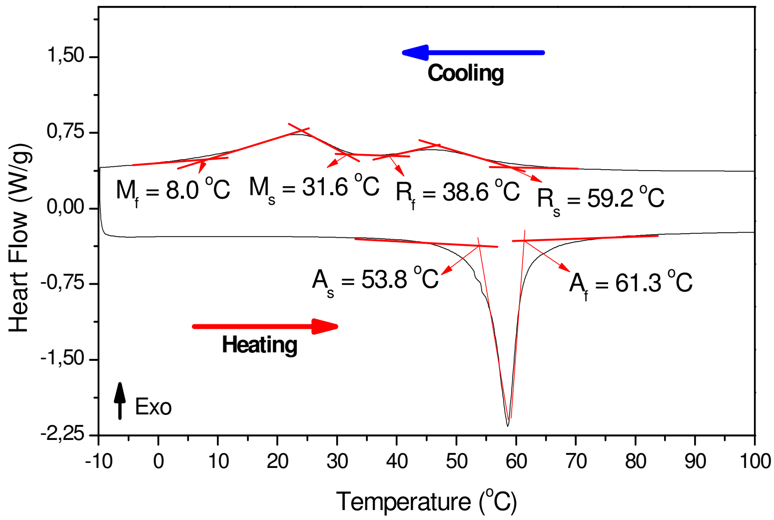


Figure 2. DSC behavior of the heat-treated Ni-Ti SMA wire.

Table 1.Transformation temperatures of the heat-treated Ni-Ti SMA wires obtained by DSC.

Sample	**Treatment**	**Transformation Temperature**					
		R_s (°C)	**R_f (°C)**	**M_s (°C)**	**M_f (°C)**	**A_s (°C)**	**A_f (°C)**
Ni-Ti wire	**450°C/ 20min**	59.2	38.6	31.6	8.0	53.8	61.3

Figure 3 presents complete sets of DMA curves for the pure epoxy matrix during heating. It appears that the storage modulus gradually decreases until 90 °C and more rapidly from this temperature, leading to the appearance of the loss factor (tan δ) peak used to determine the T_g temperature as 118.9 °C. It is noteworthy that the storage modulus and loss factor are respectively proportional to the stiffness and damping of the intrinsic material (Menard, 2007).

Figure 4 clearly shows the increase of stiffness (modulus) during the phase transformation by heating of the Ni-Ti SMA wire. Initially the modulus is approximately 30 GPa in the martensite phase and starts to gradually increase (from 67 °C) to reach a value of 70 GPa in the austenitic state (above 89 °C). This increase in stiffness is accompanied by a damping peak (Tan δ). This feature is peculiar of SMA, differentiated it from conventional metals (da Silva *et al*, 2010). Comparing Fig. 4 and Fig.2, it appears that the reverse transformation temperatures determined by DMA are higher than those observed in DSC (13 °C for A_s and 27 °C for A_f). Similarly, Batalu et al (2006) observed transformation temperatures during heating higher (average 20 °C) using DMA compared with DSC. This difference was attributed to the stabilization of the thermal and mechanical properties of the two techniques, which measure different properties using different sample sizes.

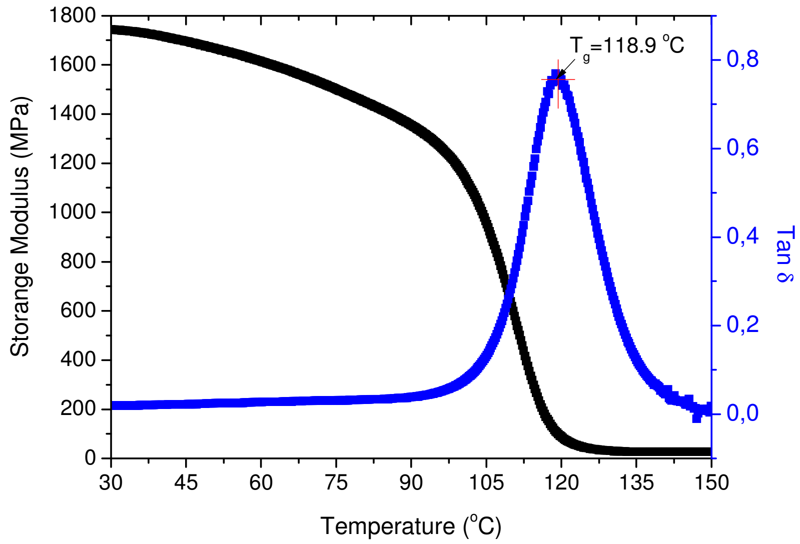


Figure 3. Storage modulus (E') and loss factor (tan δ) as a function of temperature for the epoxy system cured with TETA hardener at room temperature.

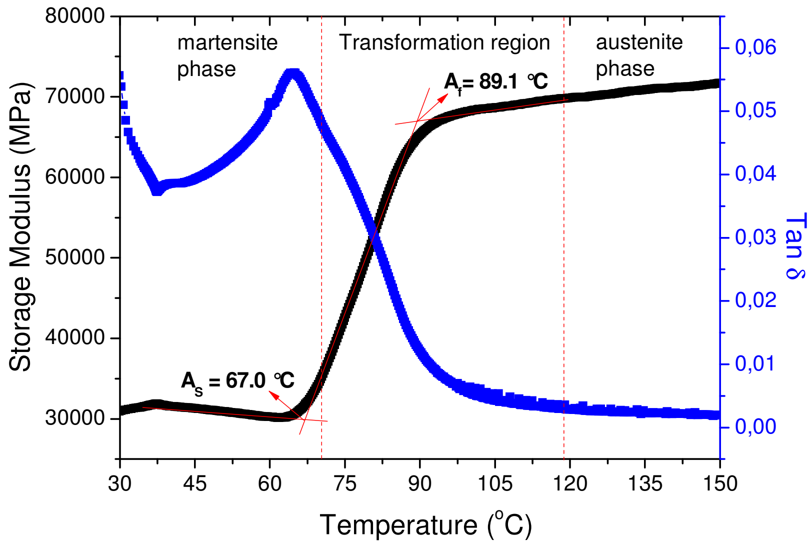


Figure 4. Stiffness and damping behavior of the Ni-Ti SMA wire.

Figure 4 also confirms the better damping capacity of martensite phase in comparison with austenite. The average value of tan δ begins at 0.05 in martensite phase and, after the peak of phase transformation, this value tends to zero in the austenite phase.

Comparing Figures 3 and 4 it is clear that in the temperature range between 30 and 90 °C, for which the epoxy resin loses rigidity, the Ni-Ti SMA wire double its module. This is the physical basis for the formation of the active composite with potential for controlled recovery of stiffness as a function of temperature.

The effect of Ni-Ti SMA wire contents on the storage modulus was investigated as shown in Fig. 5. It was verified that the storage modulus of the epoxy-SMA composites are largely affected by SMA wire content. In the single epoxy bulk (EPX_TETA), the storage modulus decreases almost linearly with the temperature until 90 °C. However, addition of 3.8 % in volume of Ni-Ti SMA wire into the EPX_TETA epoxy results in a considerable increment of storage modulus of the composites at 30 °C. During heating, the stiffness of the composite gradually decreases until the A_s temperature of Ni-Ti SMA wires is reached (Fig. 4), initiating a recovery process of the module and characterizing system activity. Between 80 and 100 °C, the system returns to the almost the same initial stiffness. This is mainly because the stiffness of Ni-Ti SMA wires becomes large after the phase transformation from martensite to austenite and it contributes to the behavior of storage modulus in epoxy-SMA composites.

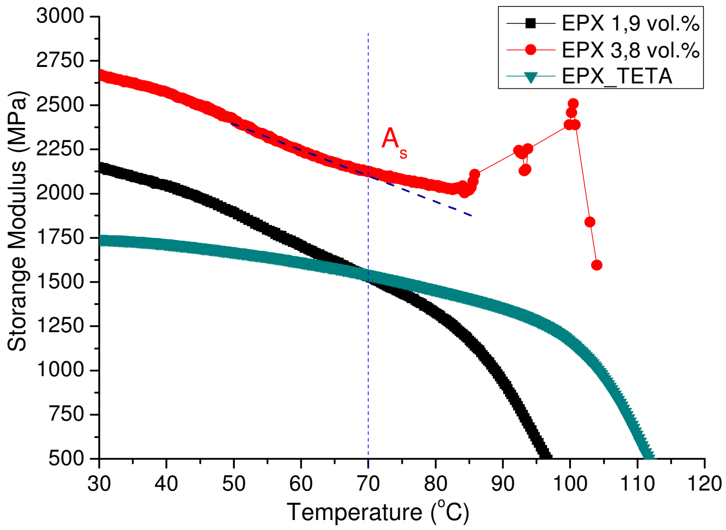


Figure 5. Storage modulus as a function of temperature for the pure epoxy system and active composites with different volume fractions of Ni-Ti SMA wires.

For the intermediate value of 1.9 vol.% of Ni-Ti SMA wires, there is an increase in initial stiffness at 30 °C, which jumps from 1.75 GPa to 2.15 GPa However, this stiffness is reduced gradually during heating of the composite and no effect due to transformation of Ni-Ti wires was observed. This behavior was also observed by Ni et al. (2007), which suggested that the ideal content of SMA wires for the effect of phase transformation is observed during heating in a polymer matrix-based epoxy resin, occurs when its volume fraction is slightly higher than 3.5 %, sufficient to cause changes in important properties such as hardness, storage modulus and the natural frequency of composite structure.

The loss factors of the epoxy-SMA composites are shown in Fig. 6. It appears that between 30 and 80 °C the damping behavior of the composite is improved compared with pure epoxy resin. This is due to higher damping capacity of martensite phase of Ni-Ti SMA wires, as shown in Fig.4. After the temperature of 80 °C there is formation of a peak that, in the case of pure epoxy resin and composite with 1.9 vol.% of Ni-Ti SMA wires, is due to approaching T_g of epoxy resin. In the case of active composite with 3.8 vol.%, the formation of damping peak occurs due to phase transformation of the Ni-Ti SMA wires.

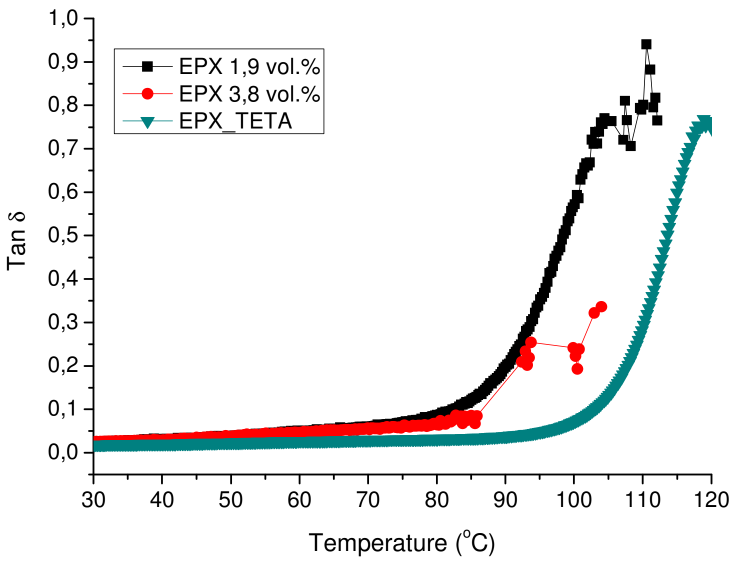


Figure 6. Loss factor (tan δ) as a function of temperature for the pure epoxy system and active composites with different volume fractions of Ni-Ti SMA wires.

5. CONCLUSIONS

The preliminary results presented in this work suggest that the behavior of the storage modulus as a function of temperature in epoxy composites during heating can be improved by the addition of small amounts of SMA wires. The addition of 3.8 vol.% of Ni-Ti SMA wires content to composite have resulted in the maximum increment of storage modulus. Moreover, when small amounts of SMA were incorporated into the epoxy matrix, as for example 1.9 vol.%, no effect was observed because the volume fraction was not enough for the phase transformation of the SMA wires act on the composite. Finally, these results have confirmed that development of smart composites may be expected by using embedded SMA wires in polymeric matrix. In future work is important to improve the thermal stability of polymeric matrix to reduce the loss of rigidity during heating in the range of phase transformation of SMA reinforcement.

6. ACKNOWLEDGEMENTS

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brazilian office for sponsoring the research (Casadinho grant 620091/2008-8 and INCT grant 574001/2008) during the course of these investigations.

7. REFERENCES

Batalu, D., Guoqiu, H., Aloman, A., Xiaoshan, L. and Zhihua, Z. 2006. "Determination of some mechanical properties of TiNi (50.6 at. % Ni) shape memory alloy using dynamic mechanical analysis and tensile tests". *Journal of Optoelectronics and Advanced Materials*, Vol. 8, pp. 694 – 698.

Da Silva N.J, Grassi E.N.D and de Araújo C.J. 2010. "Dynamic Properties of NiTi Shape Memory Alloy and Classic Structural Materials: A Comparative Analysis". *Materials Science Forum*, vol.643, pp. 37 - 41.

De Araújo, C, J., Rodrigues, L. F. A., Coutinho, N. J. F., Reis, R. P. B., 2008. "Fabrication and static characterization of carbon fiber reinforced polymers with embedded NiTi shape memory wire actuators". *Smart Materials and Structures* v.17, p 065004.

Lau, K., Zhou, L. and Tao, X., 2002 "Control of natural frequencies of a clamped–clamped composite beam with embedded shape memory alloy wires". *Composite Structure,* Vol. 58, pp.39-47.

Menard, K. 2007. "Dynamic Mechanical Analysis: A Practical Introduction". 2º ed. CRC Press, Boca Raton. 205p.

Michaud, V. 2004 "Can Shape Memory Alloys and their Composites be smart?". *Scripta Materialia*. Vol. 50 pp. 249-53.

Neuking, K., Abu-Zafaria, A., Eggler, G., 2008. "Surface engineering of shape memory alloy/polymer-composites: improved adhesion between polymers and pseudoelastic shape memory alloys". *Journal of Materials Science.* Vol.11, pp.481-2.

Ni, Q.Q., Zhang, R. X., Natsuki, T., Iwamoto, M., 2007. "Stiffness and vibration characteristics of SMA/ER3 composites with shape memory alloy short fibers". *Composite Structures*. Vol.79, pp. 501- 507.

Otsuka K, Wayman, C. M.., 1998. "*Shape Memory Materials"*, Cambridge University Press, Cambridge, UK, 284p.

Raghavan, J., Bartkiewicz, T., Boyko, S., Kupriyanov, M., Rajapakse, N. and Yu, B., 2010."Damping, tensile, and impact properties of superelastic shape memory alloy (SMA) fiber-reinforced polymer composites". *Composites*, Vol. 41, pp.214-22.

Su, W. F., Huang, H. W., Pan, W. P,. 2002. "Thermal properties of rigid rod epoxies cured with diaminodiphenylsulfone and dicyandiamide". *Thermal Acta.* Vol. 392, pp.393-4.

Vilar, T. Z., De Araújo, C. J., Reis, R. P. B., 2010. "Thermal activation of CFRP with embedded NiTi shape memory wires". *Materials Science Forum*, Vol. 643, PP. 19-28

8. RESPONSIBILITY NOTICE