LOW TEMPERATURE MOULDING OF ADAPTIVE COMPOSITES WITH EMBEDDED SHAPE MEMORY ALLOY WIRES

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ABSTRACT

The feasibility of using a low temperature liquid composite molding technique to produce smart composites with embedded shape memory alloys was investigated. The epoxy system of EPON 828 resin and DETA hardener was evaluated, with embedded NiTiCu shape memory alloy wires. For successful low temperature processing, the wires must be maintained below the austenitic start temperature, A_s, during processing and a suitable post-cure profile must be developed that results in a final epoxy glass transition temperature, T_g, that is above the peak activation temperature of the SMA wire. A cure of 24 hours at room temperature, followed by a two stage post-cure at 45°C for 6 hours and 75°C for 45 minutes, produced excellent results. This post-cure profile produced a final epoxy glass transition temperature of 97°C, and suitable mechanical properties. Stresses were evaluated during cure and post-cure with clamped or unclamped SMA wires using Fibre Bragg Gratings. This progressive cure cycle generates composites with reproducible activation behaviour, even with unclamped wires.

1. INTRODUCTION

Shape memory alloy (SMA) integration as thin wires into host composite materials is reaching potential applications as actuator and damping devices in a variety of industries, including aerospace, civil and automobile [1]. The actuation capabilities of SMAs are due to their shape memory effect: if an SMA wire is initially pre-strained while in the low temperature martensitic state, the wire recovers its initial shape upon heating. If constrained (for example in a polymer matrix), the wire cannot recover its shape and generates high recovery stresses, which lead to shape change or changes in vibration frequency of the composite [1-3]. Following this concept, adaptive composites have been manufactured in the past ten years, for example including NiTiCu alloy wires into epoxy based composites, and demonstrated their activation efficiency [4,5]. However, scale-up of the manufacturing technique for practical applications is still prevented by the need to maintain the wire pre-strain by an external frame during cure of the epoxy, to prevent them from contracting when the part temperature is above the transformation temperature of the SMA. It is however necessary that the final glass transition temperature of the composite matrix be higher than the transformation temperature of the SMA wires, in order to ensure a reliable activation.

This article presents the development of a multi-step, low temperature liquid composite moulding technique for structural smart composites with embedded pre-strained shape memory alloy wires which alleviates the need to maintain the wire pre-strained during cure. The potential influence of this technique on the composite internal stress was evaluated using optical fibres with Bragg Grating sensors.

2. MATERIALS AND EXPERIMENTS

2.1 Materials

The matrix was a standard epoxy resin, EPON 828 LVEL (Shell), mixed with a low temperature cure hardener, DETA from Sigma Aldrich (100:12 by weight ratio). Ternary NiTiCu (10.58%) wires were chosen due to their suitability for actuator behaviour in adaptive composites: they possess a relatively small transformation temperature hysteresis, which facilitates activation control, and stable cyclic behaviour, which renders them attractive for long-term applications. The NT-H8 150 μm diameter wire, from Furukawa Electric Japan, was chosen because previous work [6] has shown that it exhibits a two-way shape memory effect of 1.2% in its as-received martensitic state, which renders activation without additional prestrain possible. Additionally, its rough oxide surface favours strong interfacial bonding with the epoxy matrix. Table 1 provides some data concerning these wires.

Table 1 : Select HT-H8 SMA Wire Properties

	Value	*Unit*	*Source*
Density	6.4	g/cm^3	Furukawa
Specific Resistance	0.5 – 1.1	10^{-6} Ω•m	Furukawa
Melting Point	1240 – 1310	°C	Furukawa
Tensile Strength	1239	MPa	Baltá, 2003
Young's Modulus (initial)	19	GPa	Baltá, 2003
Linear Expansion Coefficient	10	10^{-6}/°C	Furukawa
Restorable Deformation	5 - 6	%	Furukawa
Elongation at Break	7.1	%	Baltá, 2003
Specific Heat	230 - 314	J/(kg•K)	Furukawa
Austenitic Start Temperature, A_s	59.8	°C	Kirkby, 2006
Austenitic Finish Temperature, A_f	65.6	°C	Kirkby, 2006
Martensitic Start Temperature, M_s	53.6	°C	Kirkby, 2006
Martensitic Finish Temperature, M_f	47.1	°C	Kirkby, 2006

Finally, Bragg gratings with a gauge length of 4 mm were written in silica fibres SMF-28e® from Corning. Before UV irradiation, the optical fibre acrylate coating was chemically removed along 10 mm in the FBG zone. After fabrication, the FBG sensors were pre-annealed at 100 °C during 24 hours, since the post-cure temperature of the resin is 75°C. This pre-annealing is necessary, in order to ensure the Bragg wavelength temperature stability.

The variation of the reflected light wavelength by the FBG during cure and post-cure was monitored using an optical sensing interrogator sm125-500 from Micron Optics Inc. Bragg wavelength was recorded at 0.033 Hz. This device uses a tunable multi-mode fibre laser with a 'quasi un-polarized' light output. K-type thermocouples were used to monitor the temperature.

2.2 Experiments

Pure epoxy samples

Epoxy and hardener were stirred vigorously by hand for two minutes and then degassed for a minimum of 15 minutes under vacuum at room temperature. The mixture was then cast and cured at room temperature for 24 hours. Several post-cure procedures were then carried out to study their influence on the thermal and mechanical properties of the material. Table 2 summarises the post-cure profiles studied. The goal was to

progressively reach a final glass transition temperature above 80°C, while keeping adequate matrix ductility.

Table 2 : Temperature post-cure profiles

		1st post-cure		2nd post-cure		3rd post-cure	
	Code	Temp.	Time	Temp.	Time	Temp.	Time
Post-cure profile 1	PC1	35°C	24 h	-	-	-	-
Post-cure profile 2	PC2	45°C	24 h	-	-	-	-
Post-cure profile 3	PC3	45°C	6 h	75°C	45 min	-	-
Post-cure profile 4	PC4	45°C	6 h	75°C	45 min	95°C	12 min

DSC measurements on pure resin

A TA Instruments DSC Q100 machine was used for all DSC testing performed. A heating/cooling rate of 5°C/min was used; this value was chosen to match the heating rate used in post-cure operations.

Tensile testing of epoxy

A custom-made metallic mould was used to fabricate standard dog-bone samples (ASTM D638, Type I) for tensile testing, with a cross sectional area of 40 mm^2 (~10 mm width, ~4 mm thick). It was possible to fabricate eight dog-bone samples at one time. An UTS tensile machine was used, with an extensometer, Type 411.S03 to measure the sample strain during testing, with a gauge length, LE, of 50 mm. A 100 kN load cell was used and the sample was loaded with an initial force of 10N to prevent buckling. Test speed was 1mm/min, and at least three samples were tested for each sample batch.

Epoxy-SMA composite pull-out test samples

In a second step, test samples were produced with embedded NiTiCu wires. First, single wire pull-out test samples were prepared using cylindrical silicone moulds of 10 mm in diameter and 5 mm in height, as shown in Figure 1. A wire was threaded by a needle through the centre of one mould (yellow line superimposed on Figure 1a) and aligned using a second identical mould, positioned directly above. Samples were cured in the moulds for 24 hours at room temperature, subsequently broken out of the mould and subjected to post-cure operations prior to testing. A small slice (<1 mm) was then removed from the base for DSC testing. The remaining sample was used to measure the force required to pull out the SMA wires from the epoxy matrix.

Figure 1b depicts the resulting sample, with a radius of 5 mm and a l_{emb} that varied between 3.2 mm and 4.3 mm.

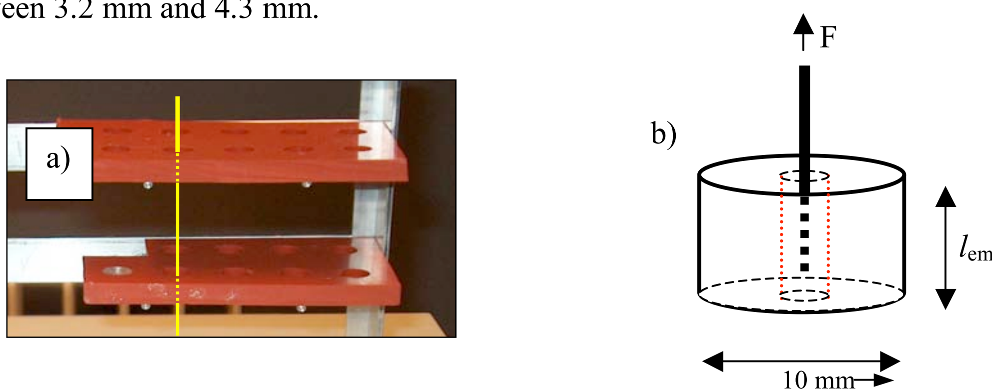

Figure 1 : a) Silicon mould for pull-out test sample preparation; b) resulting sample.

In order to characterise the interfacial bonding strength of the wire/epoxy interface, a single wire pull-out test was performed. As with the tensile testing of the pure epoxy samples, a speed of 1mm/min was used for pull-out testing. A 100 N load cell was employed; no preloading was applied. The maximal force was recorded, as well as the embedded length of each sample.

SMA-epoxy composite manufacturing
SMA/epoxy composites were used to test the activation behavior of the embedded wires and to investigate the debonding temperature of the wires in the epoxy matrix. Specimen having dimensions of 150 mm x 10 mm x 1.0 mm were made in the metallic mould presented in Figure 2. The mould was cleaned with acetone prior to moulding and treated with demoulding agent (Frekote® 770-NC from Loctite®).

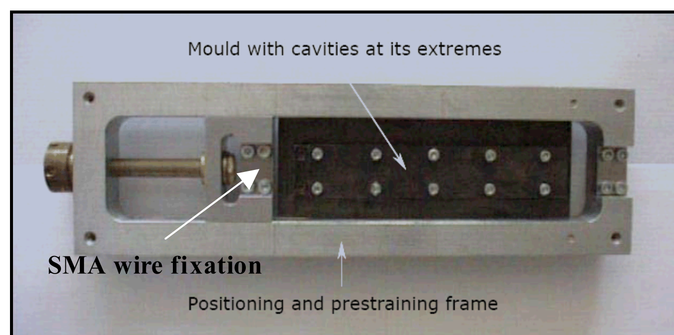

Figure 2 : Multiple wire SMA/epoxy composite mould

The outside frame was used to position and maintain the wires. For some samples a fibre Bragg grating sensor was embedded to monitor the internal strain during cure and post-cure. For these samples, 4 unstrained SMA wires were used (two at each sides of the optical fibre). For the other specimens, 6 evenly-spaced SMA unstrained wires were embedded. Specimens were cured in the steel mould at room temperature for 24 hours. Following this, the samples were post-cured in the steel mould using the most promising post-cure cycle; the samples could not be de-moulded because they were too brittle, however, the wires were left unclamped during post-cure. In one case only, with a FBG sensor, the SMA wires were left clamped during post-cure. Figure 3 is a schematic of the cured sample containing the 6 embedded wires, with thickness ranging from 0.7 mm to 1.0 mm.

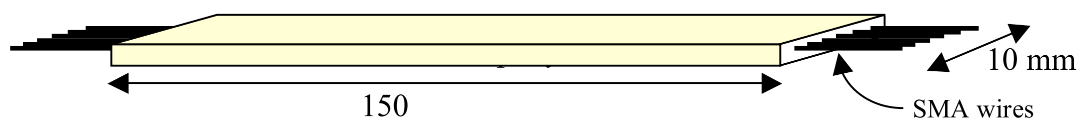

Figure 3 : Schematic of *SMA/epoxy composite*

3. EXPERIMENTAL RESULTS

3.1 Epoxy glass transition temperature after post-cure

DSC was performed on the uncured resin to measure the total heat flow associated with the cure process. The uncured samples were tested an hour after initial mixing or the

resin and hardener, due to the time of mixing and degassing. The total heat output measured was 358 J/g.

The Tg of the cured samples was then measured for the various post-cure schedules given in Table 1. The values are reported in Table 3.

Table 3 : Glass transition temperatures (T_g) results

#	*Post-cure*	*Tg (°C)*
-	Cured	48.2 ± 0.1
PC1	Post-cure profile 1	50.8 ± 3.3
PC2	Post-cure profile 2	55.6 ± 0.1
PC3	Post-cure profile 3	97.5 ± 0.4
PC4	Post-cure profile 4	110.7 ± 1.4

We observe that the glass transition temperatures for PC1 and PC2 are far too low for smart composite application. The analysis of the results of PC3 and PC4 are more relevant to the goals of the project. For such samples, a clear glass transition temperature was seen and the values recorded far exceed that of the top activation temperature of the wires at 80°C. Thus, both post-cure profiles #3 and #4 fulfil the requirements of raising the T_g sufficiently so as to prevent softening of the matrix during SMA wire activation. For PC4, the resin was cured to 97% completion according to the residual exothermicity observed.

3.2 Epoxy mechanical properties after post-cure

The samples were cast in a metallic mould prepared for dog-bone samples. Following the 24 hour cure time at room temperature, samples proved to be far too brittle to be removed in one piece from the mould and subjected to individual post-cure temperatures. Therefore, the samples were also post-cured in the mould. Based on the DSC results, only PC3 and PC4 were chosen for the test. Four dog-bone samples were prepared for each profile, but the samples containing defects such as air bubbles were discarded. Figure 4 depicts the tensile behaviour for samples post-cured using PC3 and PC4. A strain rate of 1 mm/min was used, with a perforce of 10 N (speed also 1mm/min) and a 75% F_{max} rupture criterion.

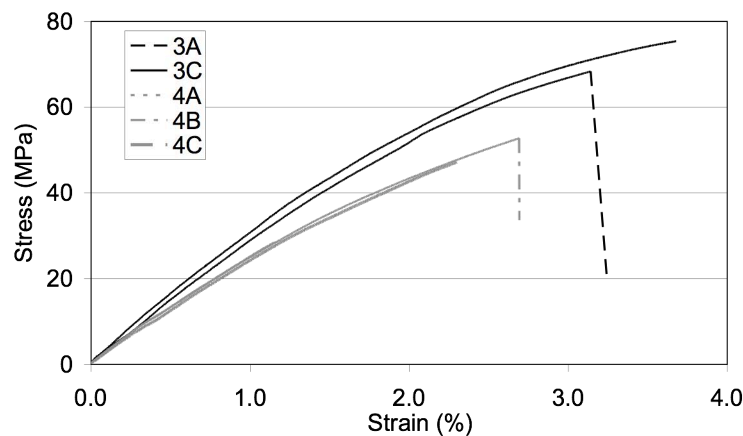

Figure 4 : Stress vs. strain curve for resin post-cured using PC3 and PC4

All samples exhibit a brittle behaviour, as would be expected. It is also observed that the post-curing to 95°C, as in profile 4, reduces the modulus of elasticity. Additionally, samples post-cured to 75°C (PC3) show overall higher tensile strength and ductility, although the statistical validity of this statement cannot be verified by only two samples. According to the manufacturer, the tensile strength of EPON 828 using DETA hardener is 75MPa, when cured at room temperature to the gel point and post-cured at 100°C for 2 hours. Sample 3C, which was defect free, had a tensile strength of 75 MPa, which is in agreement with listed values.
The properties are reported in Table 4.

Table 4 : Tensile properties of post-cured resin

	F_{max} (N)	σ_{UTS} (MPa)	ε (%)	E_{mod} (GPa)
Profile 3	2.85 ± 0.21	71.9 ± 5.0	3.5 ± 0.3	2.81 ± 0.09
Profile 4	1.68 ± 0.49	42.8 ± 12.7	2.1 ± 0.8	2.29 ± 0.04

Although more tests would increase the statistical validity, there is undoubtedly a deterioration of tensile properties when higher post-cure temperatures are used. Hence, PC3 seems to provide a good compromise.

3.3 Interfacial shear strength

Pull-out tests were performed for the four post-cure scenarios, using a constant embedded length of 3.6 mm. The maximum force was recorded, as in ref. [6] and translated into experimental interfacial shear strength by dividing it by the total interfacial area.

$$\tau_{exp} = \frac{F_{max}}{2\pi r l_{emb}} \quad [1]$$

Figure 5 reports these values. It is observed that samples manufactured with PC1 and PC2 have weak interfacial strength, in comparison to higher temperature post-cures.

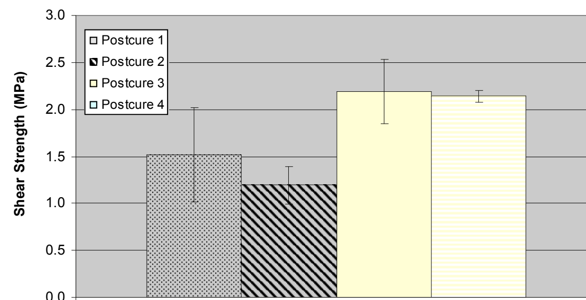

Figure 5 : Effect of post-cure profile on measured experimental interfacial shear strength.

Despite the possible influence of sample preparation on the measured interfacial shear strength, it was decided to repeat pull-out testing for PC3 and PC4 only, based on results from prior DSC testing and tensile testing of the pure epoxy.
Four samples were prepared for each post-cure profile. An average experimental interfacial shear strength of 3.6 MPa +/- 0.3 MPa was measured for profile 3; a significantly lower average of 2.8 MPa +/- 1 MPa was recorded for profile 4. The increase in these values of interfacial shear strength when compared to original testing

(Figure 5) is attributed to the smaller values of embedded length used in the second trial (First run: PC3: 4.3mm; PC4 3.8mm; second run: PC3: 3.8mm and PC4: 3.5mm). The measured shear strength decreases as the embedded length of wire is increased, due to the fact that the interfacial shear strength is averaged over a larger length of wire.

The intrinsic interfacial shear strength was then calculated using the model of Mendels et al. [7], assuming a thermal stress occurring from the final post-cure temperature and room temperature values of the epoxy modulus [8]. For PC3, a value of τ_i=59.2±9.9 MPa was found, whereas for PC4, τ_i=28.7 ± 3.1 MPa. The value of PC3 is higher than the interfacial shear strength of the resin (roughly evaluated as about 42 MPa from the tensile results) indicating a very strong bond, which was observed on the failed samples, some resin remaining on the pulled wires. PC 3 was then finally selected for the rest of the study.

3.4 Activation behaviour of the SMA-epoxy samples

Samples containing 6 wires were prepared as mentioned previously, using post-cure cycle 3, and apart from some air-bubbles entrapped due to a non-optimal mould filling procedure, all samples showed a good bond between the wire and the resin after post-cure. Before testing the activation behavior of the samples, visual debonding tests were performed, to experimentally check that the interfacial shear stress during activation of the samples was below the debonding strength of the wire-epoxy system. Small slices of samples were cut and placed on a heated stage under a binocular, and heated from room temperature up to 200°C. Only those wires that were partially debonded *prior* to heating showed further debonding in the range of activation temperatures of the wire (40°C to 80°C). Debonding of fully bonded wires was seen, however, at higher temperatures – primarily at the wire edges. At a temperature of 106°C, initial debonding at the base of one wire was noted. At 180°C, all wires showed debonding at the edges. Figure 6 depicts these results.

Figure 6 : Close up of a photograph taken of a debonded wire edge at 120°C

The strain evolution in the resin during cure and post-cure was evaluated using an FBG written on an optical fibre embedded in the middle of the sample, instead of one wire. Three experiments were performed: one with pure resin only, one with the wires clamped during cure and post-cure, and one with the wires free during post-cure. The FBG peak shift was converted into strain, removing the effect of temperature following the procedure reported in ref.[9]. Figure 7 and 8 show the strain evolution for the three cases during the room temperature cure and during post-cure 3, respectively.

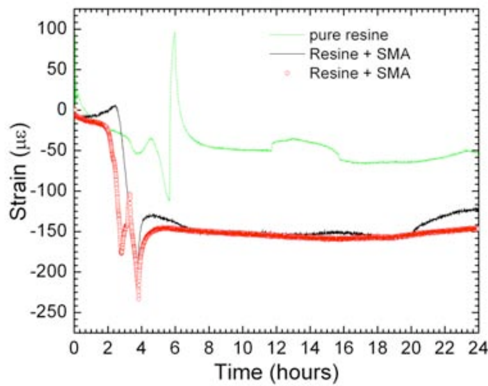

Figure 7 : Strain in the FBG sensor during cure, for pure resin, or resin with SMA.

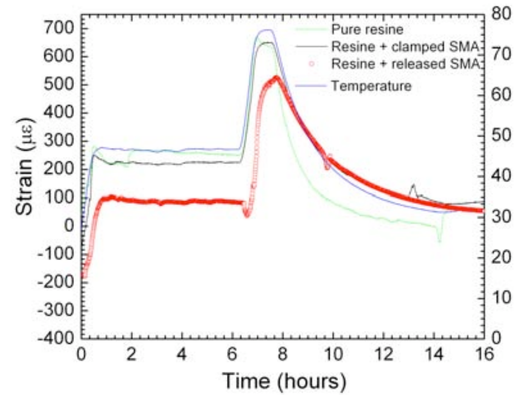

Figure 8 : Strain in the FBG sensor during post-cure, for pure resin, resin with clamped SMA wires and resin with released SMA wires.

The internal strain measurement with the FBG sensor Figure 7 indicates a slight compression for the pure resin during cure, most probably due to shrinkage after the gel time is passed (gel time is 2 to 3 hours at room temperature). For the samples with SMA wires, the compression is higher, of about -150 με. This may be due to the exothermicity of the reaction slightly raising the temperature, thus activating the wires in compression. The largest effect was observed during the post-cure, Figure 8. First, upon release of the SMA wires from the clamps, the sample with unclamped wires shows a higher compressive strain that the two other samples, most probably due to the elastic release of the wire ends. Then, upon heating, since all samples were kept in the steel mould, it is observed that the mould thermal expansion ($\alpha = 12.10^{-6}\ K^{-1}$, for steel) dominates the composite strain behaviour. Indeed, upon heating from 20 to 45°C on the first dwell, a strain of $25x12\ 10^{-6}$= 300 με is expected from the steel thermal expansion, and for the second dwell at 75°C, 660με should result. These values correspond quite exactly to the strain difference from the beginning of post-cure for all samples. For this small amount of wires, it is thus observed that the SMA wires do not exert a major role on the strain in the composite, as long as the samples are held in the mould. Upon cooling, the strains decrease, to all reach a similar value close to zero.

The samples containing no fibre optic sensor were then activated by placing them in a U-shape holder as described in ref. [5,6], and heating them through the wires by Joule effect. Figure 9 illustrates the repeated activation (4 cycles) of a SMA/epoxy composite. The 6 embedded wires were connected *in series* and the current was ramped from 0 A to 0.35 A, to obtain a peak wire temperature of 85°C. A pre-force of approximately 25 N (or ~2.5MPa) was placed on the specimen prior to testing to prevent buckling of the composite. It is important to note that by the time of testing, this composite had endured over 24 previous thermal cycles.

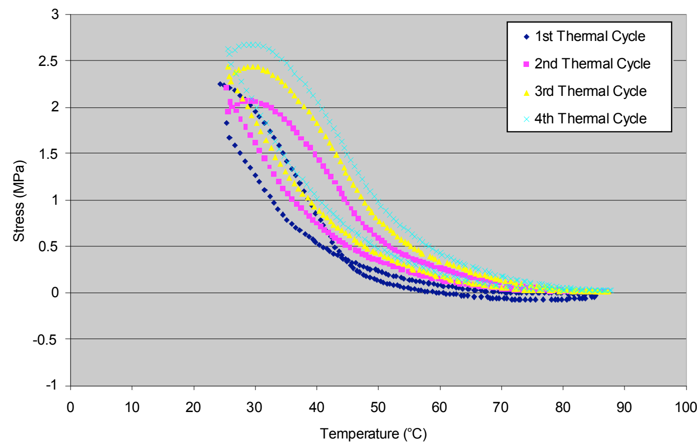

Figure 9 : Repeat activation of SMA/epoxy composite with 6 wires connected in series

Figure 9 shows that the thermal stresses of the expanding resin matrix act to reduce the stress in the clamped beam until a temperature of approximately 45°C. At this point, the wires begin to generate recovery stresses in the composite due to their 2 way shape memory effect, and counteract the matrix thermal expansion. However, due to the low SMA wire content, the recovery stresses do not completely overcome the thermal expansion of the epoxy matrix at temperatures above A_s. A higher wire content is needed in order to produce a measurable increase in recovery stress generated. In the sample tested above, the wire content is only 1.1%. It has been shown that a wire content of at least 2% is needed to generate positive overall recovery stresses in a similar epoxy system with wires pre-strained by 2 % [6]. The overall behavior of the samples is in any case very similar to that found with samples cured with clamped wires, as presented in Ref. [6].

6. CONCLUSIONS

The goal of this work was to develop a low temperature liquid composite moulding technique for smart composites with embedded shape memory alloy wires. The critical aspects were to ensure that the wires did not need to be held during curing ($T_{cure} < A_s$) and that they remained bonded in the epoxy matrix during subsequent post-cure stages and during activation.

Four different post-cure profiles were investigated and the resulting mechanical, thermal and interfacial strength of the composite were quantified. Based on the results, a cure at room temperature for 24 hours followed by a two stage post-cure, initially at 45°C for 6 hours, then at 75°C for 45 minutes, was chosen. This post-cure profile met all the requirements listed above and produced excellent results, including a final glass transition temperature of 97°C, which is above the peak activation temperature of the wire of 80°C, excellent mechanical properties (σ_{UTS} = 75 MPa) and a high interfacial strength. It was also shown with the help of FBG sensors that the strain in the matrix during post-cure is not much affected by the presence of the free wires. However, this should be verified for a composite that is not held in the mould and with a higher fraction of pre-strained wires. Large-dimension composites did not show any evidence of debonding during direct composite heating (visual test) or during wire activation from room temperature to 80°C. Finally, activation of the SMA wires showed that an expected activation behaviour was found for all, indicating that the manufacturing route proposed here is suitable for this type of adaptive composite.

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