HEATING SHAPE MEMORY POLYMERS IN ALTERNATIVE WAYS: MICROWAVE AND DIRECT ELECTRICAL HEATING.

M. Fabré[1,2], J. Binst[2], I.A. Bocsan[1,3], C. De Smet[4], J. Ivens[1,2*]

[1]*Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, Leuven, Belgium*
[2]*Department of Industrial Engineering, Lessius University College, Sint-Katelijne-Waver, Belgium*
[3]*Department of Manufacturing Engineering, Technical University of Cluj-Napoca, Romania*
[4]*Department of Architecture Sint-Lucas, Hogeschool voor Wetenschap en Kunst, Gent, Belgium*
**jan.ivens@mtm.kuleuven.be*

Keywords: Shape memory polymer composites; fillers; direct electrical heating; microwave heating

Abstract
For the moment, shape memory polymers or SMP*s are mainly used in aerospace and medical application due to their limited mechanical properties, and small recovery speed and recovery stress. The transformation and recovery speed is significantly affected by the heating rate. One way to achieve a faster heating rate is by adding fillers; the SMP can be heated by direct electrical resistivity, microwaves or induction. Adding carbon nanotubes or* CNT*s and carbon black improves the heating rate when heating the SMPs by microwaves, but also introduced the occurrence of hot spots, limiting the usability of this method of heating. Adding up to 1.13% CNTs improved the electrical conductivity enough to allow direct electrical heating, greatly increasing the heating rate. When applying a fixed voltage to the same sample, both the evolution of the current and temperature differed during the first test from the following test runs, indicating alignment of the CNTs, resulting in a lower resistivity.*

1 Introduction
Shape memory polymers or *SMP*s are part of a class of smart materials with interesting applications in fields as diverse as medicine, aerospace and design[1,2]. Work presented at ECCM 14 [3] showed reinforcing the resin with fibre textiles increased the recovery stresses and speed, but could induce stress whitening at high deformations. This paper focuses on alternative methods of heating the SMP, more particularly microwave and direct electrical heating.

1.1 Microwave heating
Microwave heating uses the interaction between molecules and an electromagnetic field with a frequency of 0.3 to 300GHz [4]. It is a fast way to increase the temperature of a material. As an added advantage, it heats volumetrically, not only the surface, making it an interesting technique to heat SMPs. Normally, the absorption of the energy of microwaves by polymers is limited, but can be improved by adding fillers, like carbon black or carbon nanotubes [5–7].

1.2 Direct electrical heating

In direct electrical heating, an electric current is passed through the SMP, resulting in a resistive, volumetric heating of the material. Pure SMP, as most polymers, is a bad electrical conductor, but conductive fillers can be added. Examples of such fillers are carbon nanotubes or carbon black, which decreases the electrical resistivity, making the material suitable for direct electrical heating [1,8–11].

2 Materials

2.1 Shape memory polymer

The shape memory polymer used is Veriflex E45 of CRG Industries (Dayton, OH), an aromatic epoxy mixed with an aromatic amine curing agent. The two components A and B are mixed in a 100–32.34 weight ratio. Plates were made by casting or infusing the resin in a 3mm thick vertical mould cavity.

The resin is compared with the resin Veriflex VF62 of CRG Industries (Table 1). This is styrene-based and cured with Benzoyl Peroxide in a 24:1 ratio. This resin was also reinforced with one layer of a quasi-unidirectional glass fibre fabric (UDG1200) with an areal density of about 1200g/m², and a volume fraction of 13%. The transformation temperature was determined by the glass transition temperature of the cured resin using Dynamic Mechanical Thermal Analysis (TA Instruments Q800).

Resin		VF E45		VF62	
Tensile strength		76	MPa	23	MPa
E-modulus		3.2	GPa	1,24	GPa
Strain to failure		3.3	%	3,90	%
Tg:	loss modulus	45	°C	62	°C
	tan δ	53	°C	75	°C

Table 1. Properties of the epoxy and styrene-based shape memory polymer resin.

2.2 Fillers

2.2.1 Carbon nanotubes

The carbon nanotubes used are multi-walled CNTs, NC 7000, which were provided by Nanocyl (Sambreville, Belgium) dispersed in A-component. The added CNTs increase the viscosity, resulting in a thick paste. This so-called master batch was mixed with regular A component in different ratios, and then mixed with the appropriate amount of B-component. This resin was then injected in the vertical mould cavity, resulting in plates with a thickness of 3mm and concentrations in carbon nanotubes of 0.37 wt%, 0.75 wt% and 1.13 wt%.

2.2.2 Carbon Black

As a comparison, also carbon black was added. Plates were made by mixing the A-component of the resin with carbon black, mixing in the B-component and curing. Carbon black was added in concentrations of 0.5 wt%, 4 wt% and 6 wt%. Higher carbon black content could not be achieved.

3 Test methods

3.1 Thermo-mechanical shape memory cycle

The deformation-cooling-reheating cycle of SMP and SMPC samples was determined in a single cantilever beam test on small samples using thermo-mechanical analysis (TA Instruments Q800). The temperature-strain cycle and the resultant stress are shown in

Figure 1. Pure epoxy SMP specimens, specimen with 6 wt% carbon black and specimens with 1.13 wt% CNT – all 17 mm x 10 mm x 3 mm – were deformed to a strain of 10% at 50°C.

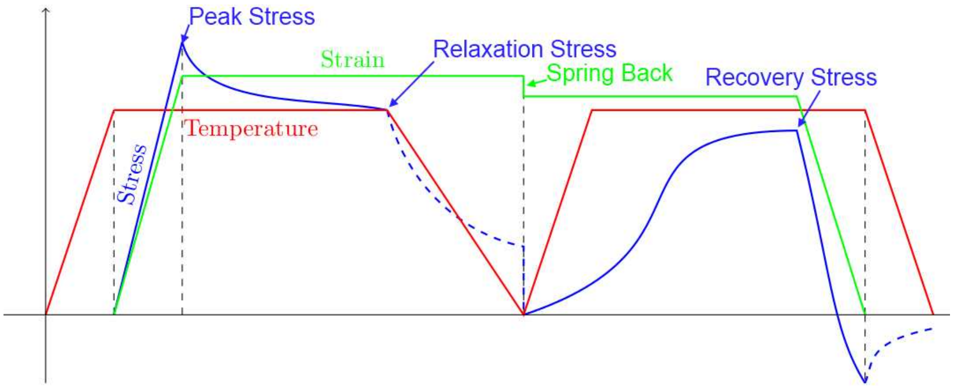


Figure 1. Temperature-strain cycle of the TMA experiments: the specimen is heated at 3°C/min to the deformation temperature. The specimen is deformed (3%/min) to a set maximum strain and held for 30 minutes to allow stress relaxation. The specimen is cooled down in deformed state. The residual stress is removed and the elastic spring back is recorded. The restrained specimen is reheated (3°C/min) to the deformation temperature, while the recovery stress is measured. Finally, the specimen is returned to the permanent shape.

These results are compared to the styrene-based SMP, both neat and reinforced with 13% fibre volume fraction of a quasi-unidirectional glass fabric (UDG1200; areal weight 1200 g/m²), which were deformed to 10% strain at 75°C.

3.2 Microwave heating

Samples of pure SMP and SMPC filled with 0.37 wt% CNT were heated in a cylindrical microwave oven, shown in Figure 2, with the wavelength of the radiation 122.5mm, a diameter of 202mm and a height of 183.7mm, or 1.5 time the wavelength. This results in a static field. For maximum heating, the sample is placed at 68mm from the bottom. The temperature of the sample was measured with a pyrometer, located at the top of the oven. The waves are generated, and enter the oven through a tunnel, where the power of the beam is measured.

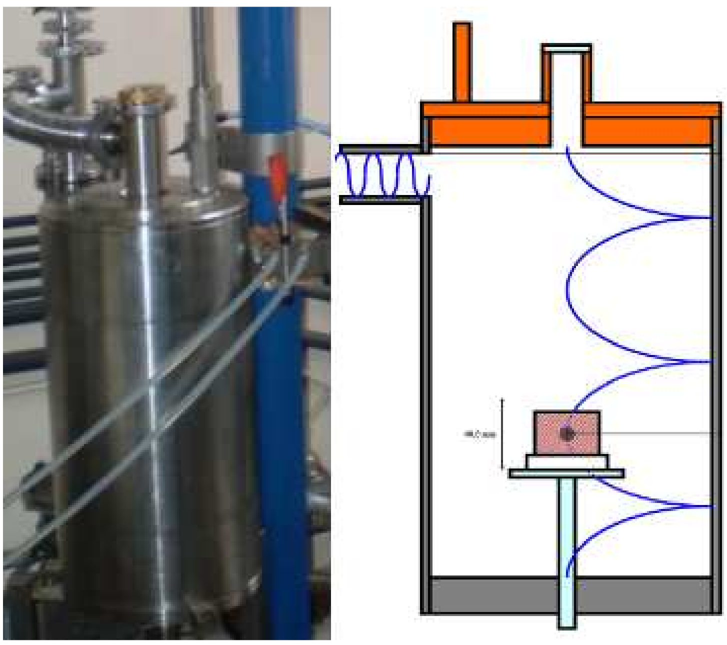


Figure 2. Microwave oven

3.3 Direct electrical heating

The electrical resistivity, capacity and inductance are first measured with a low-frequency impedance analyzer model 4192A by HP (Palo Alto, California, U.S.) through the thickness of samples measuring 20mm x 30mm x 3mm, to minimize the electrical resistance. The contact between the surface of the composite and the electrical wire is guaranteed by using conducting carbon cement. These tests were performed on the SMPC with carbon black and carbon nanotubes.

In a second set of experiments, an electric tension is applied over samples of the SMPC with CNTs, and temperature and electrical current are measured as a function of time. These tests are not performed on the SMPC filled with carbon black, because of their limited electrical conductivity.

4 Results

4.1 Shape memory cycle

Figure 3 shows an example of the thermo-mechanical cycle applied to SMP with 1.13 wt% CNT. The rise in stress at the end of the deformation cycle is due to thermal expansion, and the increased stiffness of the polymer. Table 2 contains the numerical results of the thermo-mechanical cycle applied to the different materials, also comparing them to previous results with the VF62 resin, both neat and reinforced (UDG1200). The epoxy resin performs significantly better than the styrene-based VF62, but adding CNTs or carbon black decreases the shape memory properties of the polymer. Why this happens is not clear. Research performed at other groups showed improved shape memory behaviour[1,12].

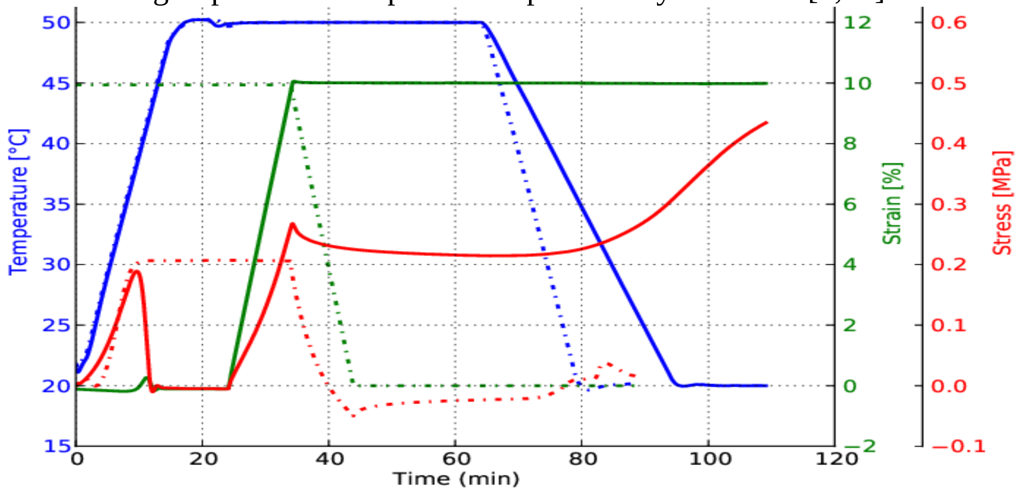


Figure 3. Example shape memory cycle of a sample with 1.13 wt% CNT. Full lines show the temperature, strain and stress during deformation, dash-dotted lines during recovery.

		Neat SMP	1.13 wt% CNT	6 wt% CB	SMP VF62	UDG1200
Resin		VF E45	VF E45	VF E45	VF 62	VF 62
Temperature	°C	50	50	50	75	75
Peak stress	MPa	0.29 ± 0.07	0.19 ± 0.04	0.16 ± 0.08	0.085 ± 0.005	2.4 ± 0.2
Relaxation stress	MPA	0.27 ± 0.05	0.15 ± 0.04	0.11 ± 0.01	0.052 ± 0.007	1.75 ± 0.12
Spring back	%	0.04 ± 0.01	0.06 ± 0.04	0.04 ± 0.01	0.025 ± 0.005	0.25 ± 0.10
Recovery stress	MPa	0.26 ± 0.01	0.12 ± 0.09	0.10 ± 0.03	0.049 ± 0.008	1.60 ± 0.06

Table 2. Comparison of the numerical data of the TMA experiments. The first 3 materials are with the VF E45 epoxy resin, the last 2 are the styrene-based VF62.

4.2 Microwave heating

Tests were first performed on samples measuring 25mm x 35mm x 3mm of neat SMP resin VF E45 at different power levels. Figure 4 shows the result of heating samples of neat SMP resin at 100W, 150W and 250W. The sharp rise of the temperature at higher power levels can be attributed to the occurrence of hot spots, where the temperature rises very locally. Warmer polymer absorbs microwave energy better[4], so this effect reinforces itself and can lead to run-away. These hotspots can be seen in Figure 5. Because of these hotspots, subsequent samples were only tested at 75W and 100W.

Samples with carbon nanotubes are more susceptible to these hotspots, as can be seen in Figure 6. This is probably caused by a non-uniform dispersion of the CNTs, which locally causes a faster heating, further self-reinforced by the increased absorption. The non-uniform dispersion of CNTs in aged master batches was also experienced by other members of the research group[13].

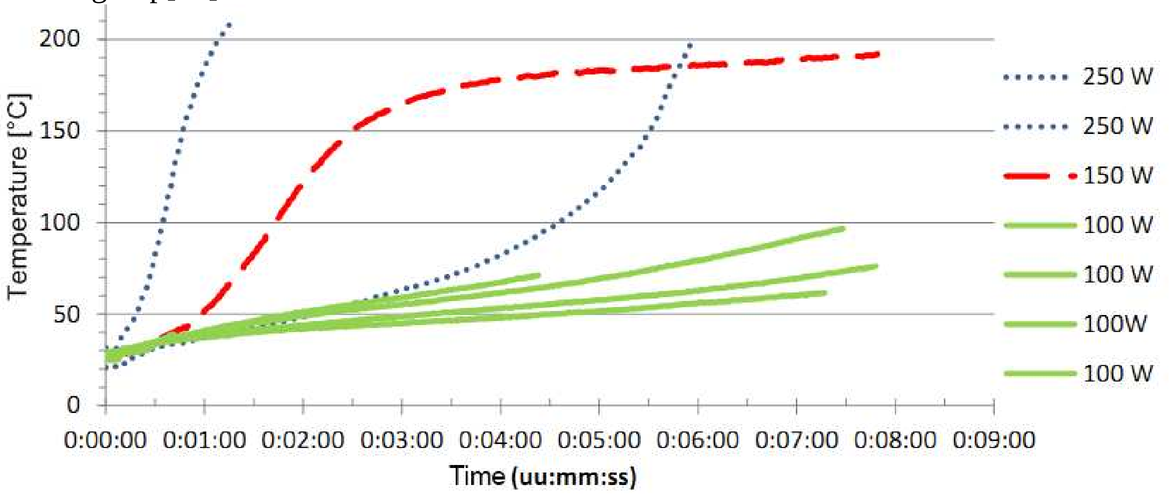


Figure 4. Temperature as a function of time for pure SMP samples undergoing microwave heating at 100W, 150W and 250W.

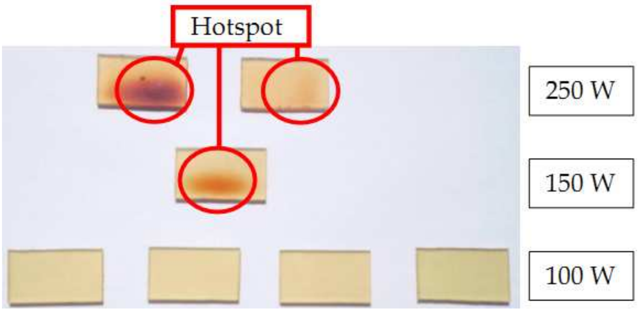


Figure 5. Hotspots resulting from microwave heating at higher power levels.

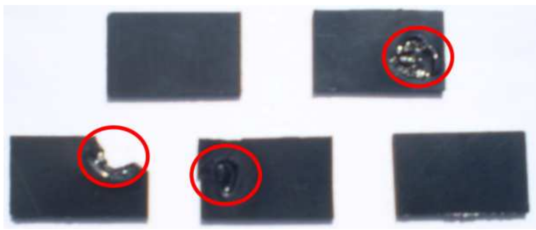


Figure 6. Hotspots occurring when microwave heating samples with 0.37 wt% CNTs at 100W

When comparing the microwave heating of pure SMP and SMPC with 0.37 wt% CNT , as can be seen in Figure 7, the SMPC heat faster, and reaches the transition temperature a minute faster. The spike at the end is the start of a hotspot.

4.3 Direct electrical heating

Figure 8 shows the electrical resistivity as measured with the impedance analyzer as a function of the filler concentration. The added carbon black doesn't have a significant effect on the resistivity, while adding carbon nanotubes significantly lowers the electrical resistivity.

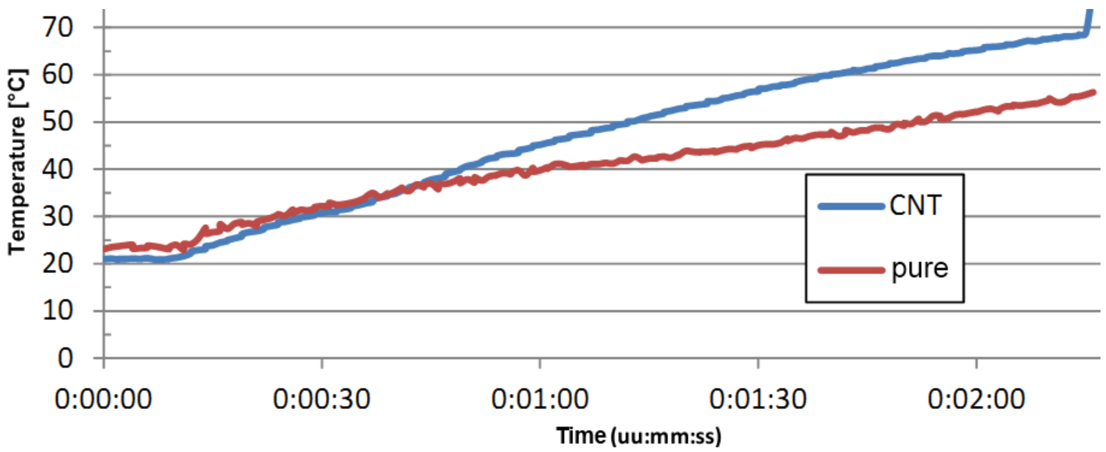


Figure 7. Comparing microwave heating of pure SMP and SMPC with 0.37 wt% CNT

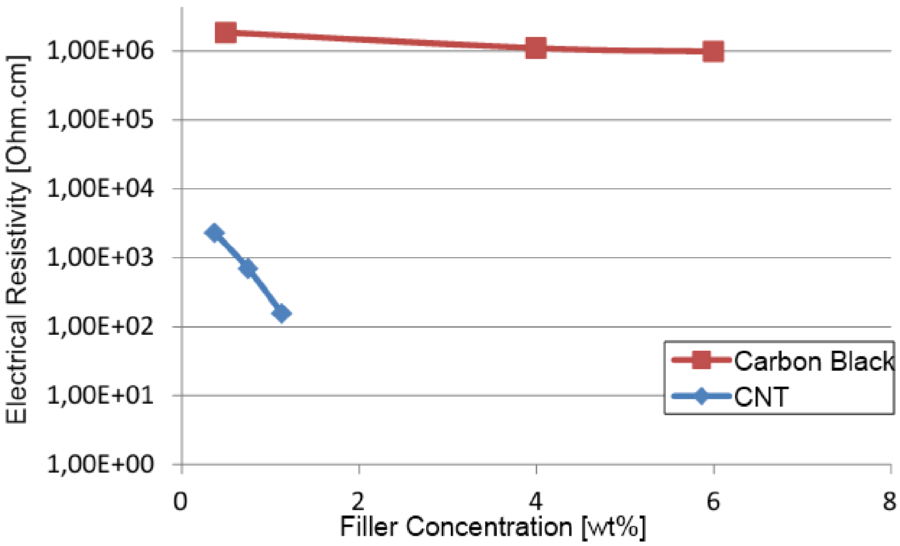


Figure 8. Electrical resistivity in function of concentration for SMPC with CNT and carbon black.

Subsequently the electrical resistivity of the SMPC with 1.13 wt% CNT was measured at different voltages. As can be seen in Figure 9, this resistivity varies over the different cycles, indicating some alignment of the nanotubes into a conducting network.

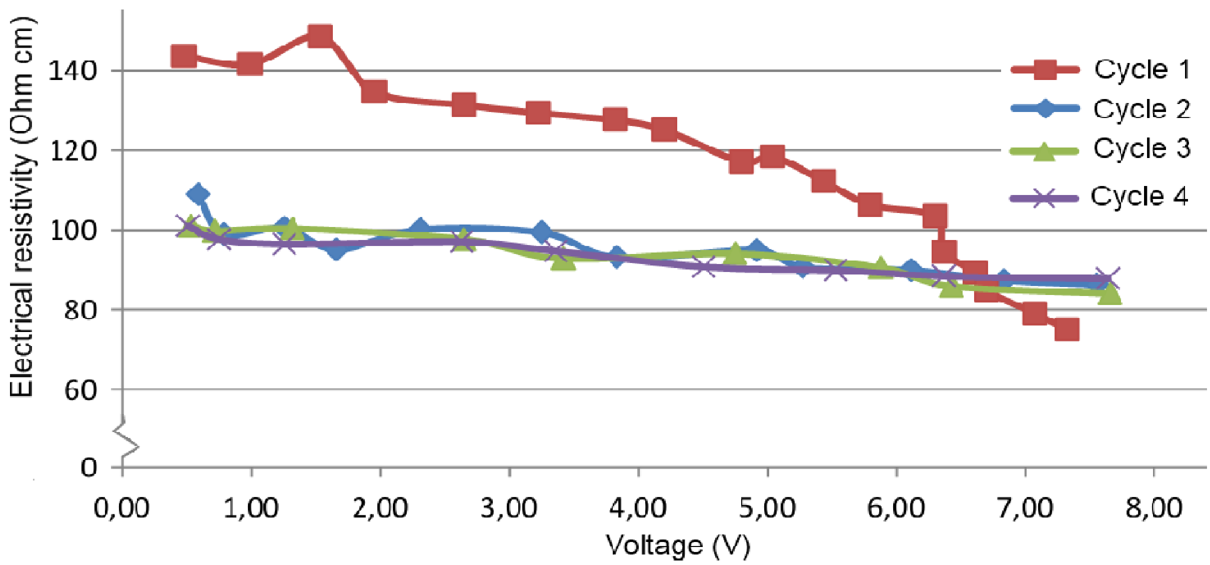
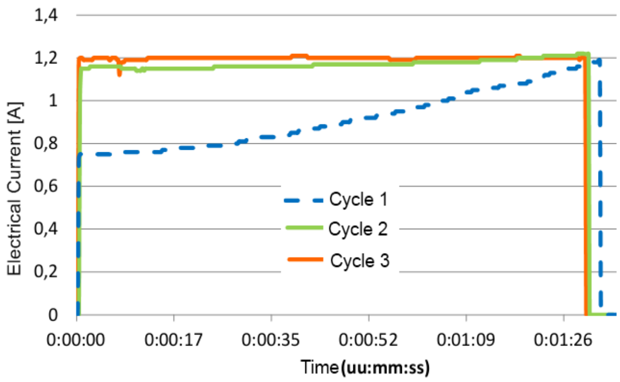


Figure 9. Resistivity as a function of voltage for SMPC with 1.13 wt% CNT. This measurement was repeated 4 times on the same sample.

To verify this effect, a tension of 5V was applied over a sample during 4 cycles of 90 seconds while monitoring the current and temperature. The result of this can be seen in Figure 10, showing an increase in current, and thus a decrease in resistivity during the first cycle. This change in electrical properties is also seen in the temperature graph, where the first cycle heats slower. Subsequent cycles have a level current and increase in temperature at the same rate, probably caused by the alignment of the CNTs, forming a conductive network.



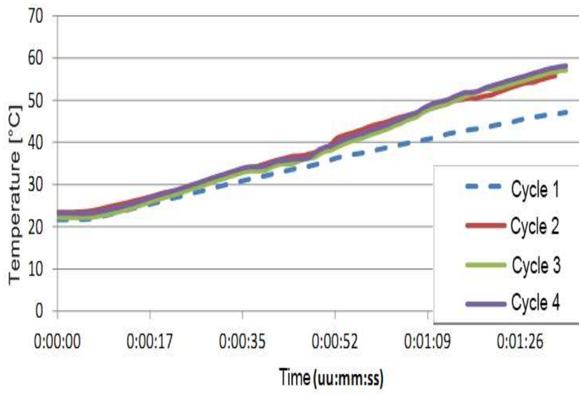


Figure 10. Electric current and temperature as a function of time while applying 5V of tension on an SMPC sample with 1.13wt% CNT.

As an illustration of the heating of shape memory polymer composites with carbon nanotubes, a sample of SMPC with 1.13 wt% CNT was subjected to a tension of 30 V DC, and photographs were taken at regular intervals. As can be seen in Figure 11, the sample starts deforming after approximately 30 s, and is fully recovered after 120s, as opposed to 200s with conventional heating[3].

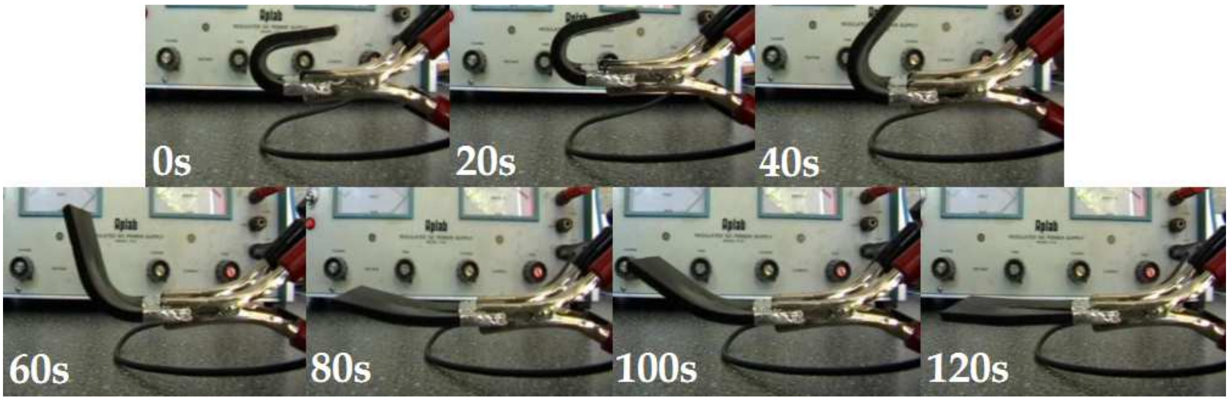


Figure 11. Time series photograph of SMPC with 1.13wt% under a tension of 30 V DC.

5 Conclusion

Adding carbon black and carbon nanotubes enables the material to be heated in different ways, opening possibilities for new applications of shape memory polymers. Microwave heating is fast, and volumetric, but local hot spots occurred during testing. Adding CNTs or carbon black increased the absorption of the microwave energy, but also the occurrence of hot spots, possibly due to an inhomogeneous distribution. The issue of hot spots needs to be solved first, before it becomes a viable option.

The fillers did not result in a improvement of the shape memory properties: compared to the neat resin, relaxation and recovery stress approximately halved when adding 6 wt% carbon black or 1.13 wt% carbon nanotubes.

Adding relatively small quantities of carbon nanotubes (0.37 wt% to 1.13 wt%) significantly increases the electrical conductivity, enabling direct electrical heating. During the first application of an electric tension, the CNTs seem to rearrange into a more conductive network, increasing the heating rate.

6 References

[1] Leng J., Lan X., Liu Y., Du S. Shape-memory polymers and their composites: Stimulus methods and applications. *Progress in Materials Science*, **56**, pp. 1077-1135. (2011).

[2] Rousseau I.A. Challenges of shape memory polymers: A review of the progress toward overcoming SMP's limitations. *Polymer Engineering & Science*, **48**, pp. 2075-2089. (2008).

[3] Ivens J., Urbanus M., Smet C. De Shape recovery in a thermoset shape memory polymer and its fabric-reinforced composites. *Express Polymer Letters*, **5**, pp. 254-261. (2011).

[4] Clark D.E., Sutton W.H. Microwave Processing of Materials. *Annual Review of Materials Science*, **26**, pp. 299-331. (1996).

[5] Liu F., Qian X., Wu X., Guo C., Lei Y., Zhang J. The response of carbon black filled high-density polyethylene to microwave processing. *Journal of Materials Processing Technology*, **210**, pp. 1991-1996. (2010).

[6] Harper J., Price D., Zhang J. Use of fillers to enable the microwave processing of polyethylene. *The Journal of microwave power and electromagnetic energy : a publication of the International Microwave Power Institute*, **40**, pp. 219-27. (2007).

[7] Fan Z., Luo G., Zhang Z., Zhou L., Wei F. Electromagnetic and microwave absorbing properties of multi-walled carbon nanotubes/polymer composites. *Materials Science and Engineering: B*, **132**, pp. 85-89. (2006).

[8] Cho J.W., Kim J.W., Jung Y.C., Goo N.S. Electroactive Shape-Memory Polyurethane Composites Incorporating Carbon Nanotubes. *Macromolecular Rapid Communications*, **26**, pp. 412-416. (2005).

[9] Leng J.S., Lan X., Liu Y.J., Du S.Y., Huang W.M., Liu N., Phee S.J., Yuan Q. Electrical conductivity of thermoresponsive shape-memory polymer with embedded micron sized Ni powder chains. *Applied Physics Letters*, **92**, pp. 014104. (2008).

[10] Leng J., Lv H., Liu Y., Du S. Electroactivate shape-memory polymer filled with nanocarbon particles and short carbon fibers. *Applied Physics Letters*, **91**, pp. 144105. (2007).

[11] Meng Q., Hu J. A review of shape memory polymer composites and blends. *Composites Part A: Applied Science and Manufacturing*, **40**, pp. 1661-1672. (2009).

[12] Ni Q.-Q., Zhang C.-sheng, Fu Y., Dai G., Kimura T. Shape memory effect and mechanical properties of carbon nanotube/shape memory polymer nanocomposites. *Composite Structures*, **81**, pp. 176-184. (2007).

[13] Gorbatikh L., Haesch A., Clarkson T., Ivens I., Lomov S.V., Verpoest I. *On localization of carbon nanotubes in woven glass fiber/epoxy composites and its effect on tensile properties.* in "Proceedings of *15th European Conference on Composite Materials*", Venice, Italy (2012)