Monitoring of curing and cyclic thermoresistive response using monofilament carbon nanotube yarn/silicone composites

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Supplementary Information

S1. Heating-dwell temperature program

A heating-dwell temperature program was used for two CNTY monofilament composites (CNTY/SR_1 and CNTY/SR_2) in this section. Figure S1 shows the schematic of this temperature program, which is divided into seven zones.

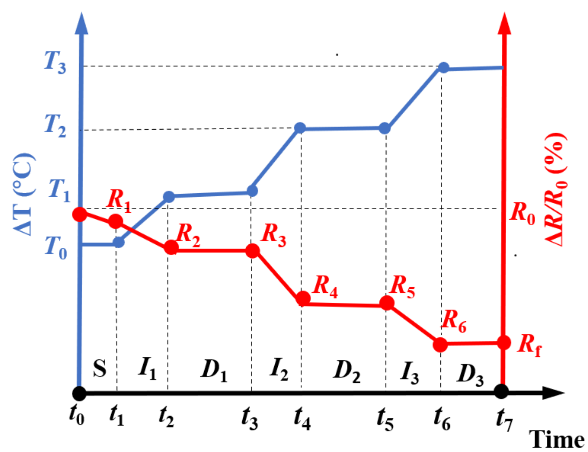

Figure S1. Heating-dwell temperature program for CNTY/SR_1 and CNTY/SR_2.

Table S1. Description of zones characterized for CNTY/SR_1 and CNTY/SR_2.

Zone	Time Interval	Electrical Resistance	Fractional Change in the Electrical Resistance		Description of Zones	Parameter
			CNTY/SR_1	CNTY/SR_2		
S	$t_0 - t_1$	$R_0 - R_1$	−0.21%	−0.06%	Stabilization zone	*SNR*
$\boldsymbol{H_1}$	$t_1 - t_2$	$R_1 - R_2$	−0.44%	−0.30%	Heating from T_0 to T_1	β_H
$\boldsymbol{D_1}$	$t_2 - t_3$	$R_2 - R_3$	−1.14%	−0.83%	Dwell at T_1	*SNR*
$\boldsymbol{H_2}$	$t_3 - t_4$	$R_3 - R_4$	−1.85%	−1.57%	Heating from T_1 to T_2	β_H
$\boldsymbol{D_2}$	$t_4 - t_5$	$R_4 - R_5$	−4.57%	−3.20%	Dwell at T_2	*SNR*
$\boldsymbol{H_3}$	$t_5 - t_6$	$R_5 - R_6$	−5.38%	−3.90%	Heating from T_2 to T_3	β_H
$\boldsymbol{D_3}$	$t_6 - t_7$	$R_6 - R_f$	−6.87%	−5.63%	Dwell at T_3	*SNR*

Table S1 shows the description of zones and the parameters characterized for the specimens in each section. The signal to noise ratio of the fractional change in electrical resistance and the thermoresistive sensitivity (temperature coefficient of resistance) were calculated according to Equations (1), (2) and (3).

Zone *S* represents the initial stabilization zone where the temperature of the oven was kept constant at RT (T_0) for 15 minutes. The fractional change in the electrical resistance at the beginning of zone *S* is denoted as R_0. In zone H_1, the temperature ramped from T_0 to T_1 (~38 °C) at a constant rate of 1.0 °C /min. In this zone, the electrical resistance decreases from R_1 (−0.21% for CNTY/SR_1 and −0.06% for CNTY/SR_2) to R_2 (−0.44% for CNTY/SR_1 and −0.30% for CNTY/SR_2). D_1 represents the dwell zone in which the temperature was held constant at 37.5 °C for 60 minutes. $\Delta R/R_0$ decreased from R_2 to R_3 (−1.14% for CNTY/SR_1 and −0.83% for CNTY/SR_2). In zone H_2, the temperature increased from T_1 (38 °C) to T_2 (60 °C), while $\Delta R/R_0$ decreased from R_3 to R_4 (−1.84% for CNTY/SR_1 and −1.57% for CNTY/SR_2). D_2 represents the dwell zone at 60°C for 60 minutes in which the resistance changes from R_4 to R_5 (−4.57% for CNTY/SR_1 and −3.20% for CNTY/SR_2). The temperature ramped from T_1 (60 °C) to T_2 (80 °C) in zone H_3, while $\Delta R/R_0$ decreased from R_5 to R_6 (−5.38% for CNTY/SR_1 and −3.90% for CNTY/SR_2). D_3 represents the dwell zone at 80 °C for 60 minutes in which $\Delta R/R_0$ changes from R_6 to R_f (−6.87% for CNTY/SR_1 and −5.63% CNTY/SR_2, respectively).

S2. Heating-dwell-cooling temperature program

In this section, a heating-dwell-cooling temperature program was used (Figure S2) to investigate the thermoresistive behavior of the CNTY/SR_1 and CNTY/SR_2 specimens. SNR values were calculated at stabilization/dwell zones according to Equation (1).

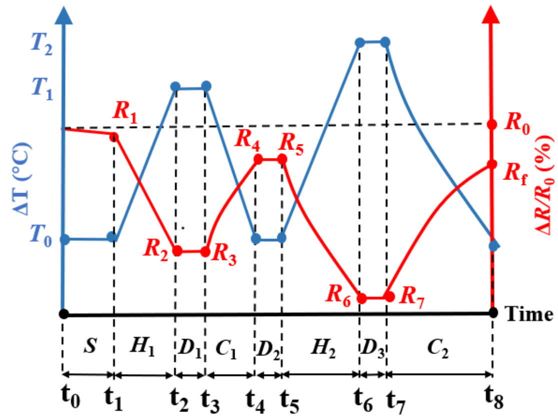

Figure S2. Heating-dwell-cooling temperature program for CNTY/SR_1 and CNTY/SR_2.

After the stabilization zone (*S*) for 15 minutes, two heating-dwell-cooling cycles were repeated for both specimens. Table S2 shows the summary of zones and parameters characterized in each section. The program was divided into two heating-dwell-cooling cycles. In the first cycle, the oven was heated from T_0 (RT) to T_1 (~35 °C) at the rate of 0.4 °C/min (H_1). $\Delta R/R_0$ decreased from R_1 to R_2 (−0.12% to −1.16% for CNTY/SR_1 and from −0.03% to −0.83% for CNTY/SR_2). The temperature of the oven remained constant at T_1 for 10 minutes (zone D_1) while $\Delta R/R_0$ had a subtle change (R_3 was −1.21% for CNTY/SR_1 and −0.93% for CNTY/SR_2). In zone C_1, the oven cooled down to T_0 at the rate of 0.05 °C /min. In this zone, $\Delta R/R_0$ varied from R_3 to R_4 (−1.41% and −0.73% for CNTY/SR_1 and CNTY/SR_2, respectively). D_2 represents the dwell zone at T_0 for 10 minutes. $\Delta R/R_0$ changed from R_4 to R_5 (−1.47% for CNTY/SR_1 and −0.75% for CNTY/SR_2). In the second cycle, the temperature raised from T_0 to T_2 (50 °C) at the rate of 0.4 °C/min in zone H_2 while the $\Delta R/R_0$ decreased from R_5 to R_6 (−3.16% and −2.29% in CNTY/SR_1 and CNTY/SR_2, respectively). The temperature of the oven was kept constant at T_2 for 10 minutes in zone D_3. $\Delta R/R_0$ had small fluctuations in this section (R_7 was −3.30% for CNTY/SR_1 and −3.30% for CNTY/SR_2). In zone C_2, the temperature was cooled down to T_0 at the rate of 0.05 °C /min. $\Delta R/R_0$ increased from R_7 to R_f (−2.24% and −1.34% for CNTY/SR_1 and CNTY/SR_2, respectively). Table S2 represents the details of the temperature program along with their corresponding fractional change in the electrical resistance measurements in each zone. Equations (2) and (3) were used to calculate the thermoresistive sensitivity of the specimens during heating/cooling sections.

Table S2. Description of zones and parameters in heating-dwell-cooling temperature cycles.						
Zone	**Time Interval**	**Electrical Resistance**	**Fractional Change in the Electrical Resistance**		**Description of Zone**	**Parameter**
			CNTY/SR₁	**CNTY/SR₂**		
S	t_0−t_1	R_0−R_1	−0.12%	−0.03%	Stabilization zone	*SNR*
$\boldsymbol{H_1}$	t_1−t_2	R_1−R_2	−1.16%	−0.83%	Heating from T_0 toT_1	β_{H}
$\boldsymbol{D_1}$	t_2−t_3	R_2−R_3	−1.21%	−0.93%	Dwell at T_1	*SNR*
$\boldsymbol{C_1}$	t_3−t_4	R_3−R_4	−1.41%	−0.73%	Cooling from T_1 to T_0	β_{C}
$\boldsymbol{D_2}$	t_4−t_5	R_4−R_5	−1.47%	−0.75%	Dwell at T_0	*SNR*
$\boldsymbol{H_2}$	t_5−t_6	R_5−R_6	−3.16%	−2.29%	Heating from T_0 toT_2	β_{H}
$\boldsymbol{D_3}$	t_6−t_7	R_6−R_7	−3.30%	−2.42%	Dwell at T_2	*SNR*
$\boldsymbol{C_2}$	t_7−t_8	R_7−R_f	−2.24%	−1.34%	Cooling from T_2 toT_0	β_{C}

S3. Heating-cooling cyclic program

Figure S3 represents a thermal cyclic program used to calculate the thermoresistive sensitivity and hysteresis of CNTY/SR_1 and CNTY/SR_2 specimens. After the stabilization zone (*S*), the samples were heated from RT to 100°C and cooled back to RT for four continuous cycles at the rate of 1.0 °C/min for both heating/cooling paths. SNR was calculated in the stabilization zone according to Equation (1).

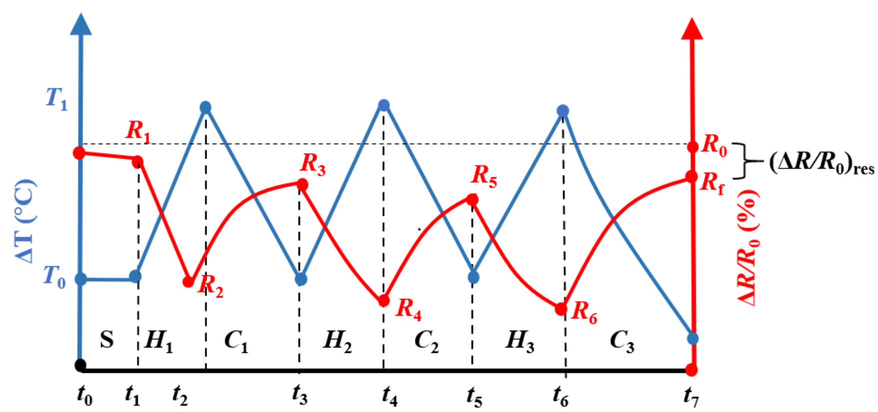

Figure S3. Cyclic temperature program for CNTY/SR_1 and CNTY/SR_2.

Table (S3) shows the description of each zone and the parameters calculated in each section. The thermoresistive sensitivity was calculated in each heating/cooling section according to Equations (1) and (2). The first cycle was not included in the calculations. In zone H_1, the temperature was raised from T_0 (RT) to T_1 (100 °C) while $\Delta R/R_0$ decreased from R_0 to R_1 (0 to −5.93% for CNTY/SR_1 and 0 to −4.96% for CNTY/SR_2). In zone C_1, the temperature cooled back to T_0, and the resistance increased from R_1 to R_2 (−0.31% for

CNTY/SR_1 and −0.47% for CNTY/SR_2). During the second cycle, the temperature increased from T_0 to T_1 in zone H_2 and $\Delta R/R_0$ decreased from R_2 to R_3 (−5.95% for CNTY/SR_1 and −4.90% for CNTY/SR_2). In zone C_2, the oven was cooled back to T_0 while $\Delta R/R_0$ decreased from R_3 to R_4 (−0.47% for CNTY/SR_1 and −0.28% for CNTY/SR_2). H_3 represents the last heating zone in which $\Delta R/R_0$ decreased from R_4 to R_5 (−6.09% for CNTY/SR_1 and −5.07% for CNTY/SR_2). $\Delta R/R_0$ increased from R_5 to R_f (−0.74% for CNTY/SR_1 and −0.36% for CNTY/SR_2) by cooling down the temperature to T_0. TCR values were calculated in heating/cooling sections and average TCR were reported according to Equations (2) and (3).

Table S3. Description of zones and parameters characterized for CNTY/SR1 and CNTY/SR2.

Zone	Time Interval	Electrical Resistance	Fractional Change in the Electrical Resistance		Description of Zone	Parameter
			CNTY/SR_1	CNTY/SR_2		
H_1	t_0−t_1	R_0−R_1	−5.93%	−4.96%	Heating from T_0 to T_1	β_H
C_1	t_1−t_2	R_1−R_2	−0.31%	−0.47%	Cooling from T_1 to T_0	β_C
H_2	t_2−t_3	R_2−R_3	−5.95%	−4.90%	Heating from T_0 to T_1	β_H
C_2	t_3−t_4	R_3−R_4	−0.47%	−0.28%	Cooling from T_1 to T_0	β_C
H_3	t_4−t_5	R_4−R_5	−6.09%	−5.07%	Heating from T_0 to T_1	β_H
C_3	t_5−t_6	R_5−R_f	−0.74%	−0.36%	Cooling from T_1 to T_0	β_C

S4. Calculation of hysteresis in heating-cooling cycles

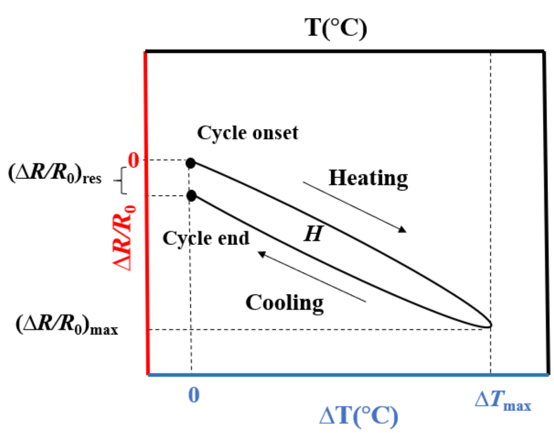

Figure S4. Parameters used for characterization of hysteresis of CNTY/SR_1 and CNTY/SR_2.

The cyclic thermoresistive behavior of each heating-cooling cycle was quantified using three experimental parameters: the residual fractional change in electrical resistance $(\Delta R/R_0)_{res}$, the maximum fractional change in electrical resistance $(\Delta R/R_0)_{max}$, and the normalized hysteresis (H_N). Figure S4 shows a schematic of a cycle and the parameters. The cycles described in section S3 were used for data analysis of each specimen. Two independent parameters were used to evaluate the normalized hysteresis: the maximum normalized change in electrical resistance $(\Delta R/R_0)_{max}$ and a dependent metric (H), which is obtained by subtracting the absolute value of area under the heating curve of each cycle from that of cooling curve. Then the normalized hysteresis (H_N) was quantified for each cycle (Equation 6) by dividing the area of the hysteresis loop (H) over the product of the maximum temperature change $(\Delta T)_{max}$ and the maximum fractional change in electrical resistance,$(\Delta R/R_0)_{max}$.

References

References list in the Supplementary Information correspond to the list of References in the main manuscript.