International Journal of Technology and Applied Science (IJTAS)

E-ISSN: 2230-9004 ● Website: www.ijtas.com ● Email: editor@ijtas.com

Temperature Dependent Electrical Transport and Thermoresistive Behaviour of CNT/Epoxy Composites for Temperature Sensor Applications

Dr. Jyoti Mishra

Assistant Professor
Department of Physics
D.B.S. College, Govind Nagar, Kanpur, U.P.

Abstract:
A cured epoxy that contains a few tenths of a percent of carbon nanotubes conducts electricity through tunnelling junctions between neighbouring tubes. Its resistance shifts with temperature, and for some years this has been put forward as a route to cheap thermometers that can be printed or cast where they are needed. The measurements in the literature do not agree with one another, however. Groups report different signs for the temperature coefficient of resistance (TCR), different magnitudes, and different behaviour around the glass transition. We look at the question with a model of two terms. One is fluctuation-induced tunnelling across the inter-tube junctions, which makes the resistance fall as the sample warms. The other is thermal expansion of the resin, which pulls the junctions open and makes it rise. We take a junction gap of 1.5 nm, a junction area of 1 nm^2 and effective barriers from 0.05 to 0.20 eV. Tunnelling by itself then gives a TCR at 300 K of between −0.03 and −0.32% K^{-1}. Expansion cuts this down. Over a threefold span of the gap-sensitivity parameter it also creates a minimum in the resistance that sits exactly at the glass transition temperature. If the expansion term is made stronger still, the minimum drops to room temperature and the composite is nearly worthless as a thermometer. The paper closes with the consequences for calibration, resolution and working range, and with a comparison against platinum resistors and thermistors.

Keywords: carbon nanotubes, epoxy nanocomposite, fluctuation-induced tunnelling, temperature coefficient of resistance, thermoresistivity, thermal expansion, glass transition, temperature sensor.

1 Introduction

Almost all resistance thermometry is done with one of two devices. A platinum resistor is stable and close to linear, but its resistance moves by under half a percent for each kelvin. A ceramic thermistor responds about ten times more strongly; the price is a steep exponential characteristic and a brittle body. Both are discrete parts, and both have to be glued or clamped to whatever is being measured. That is inconvenient in several places: inside a laminate while it cures, on a pipe with a tight curve, or across a large panel

whose temperature is wanted at many points at once. In such cases one would gladly accept a less accurate sensor if it could be painted on or cast in and then simply read as a resistor.

Epoxy filled with carbon nanotubes (CNTs) is one material that might do this. Nanotubes, which Iijima first described in 1991 [1], conduct well along their length and are typically several hundred times longer than they are wide. When they are dispersed in an insulating resin, a connected network appears at very small loadings, and thresholds far below 0.1 wt% have been reported for epoxy [2]. So little filler leaves the viscosity of the uncured resin and the mechanical properties of the cured solid nearly untouched. There is a further attraction. Epoxy is already the matrix in most structural composites and in a good many electronic encapsulants, so the sensor and the structure that carries it can be the same chemical.

The first clear demonstration came from Neitzert, Vertuccio and Sorrentino. Their epoxy with 0.5 wt% of multiwalled tubes worked as a heater and as a temperature sensor up to 160 °C, and it had a negative temperature coefficient of the kind expected from tunnelling between tubes [3]. Later work has been less tidy. Lasater and Thostenson followed the resistance of a nanotube-filled vinyl ester during thermomechanical analysis. At higher loadings they saw the TCR take either sign, and close to the percolation threshold they found a small negative value [4]. Cen-Puc, Oliva-Avilés and Avilés built a model around the thermal expansion of the polymer, and it gave a positive coefficient at every concentration they tried [5]. In fibre-reinforced laminates that contain nanotubes, Dai, Thostenson and Schumacher found more complicated behaviour again [6]. A 2025 preprint by Jafarypouria and Abaimov reports that a fully cured single-walled nanotube epoxy at about 1 wt% hardly changes its resistance at all below the glass transition, and the authors point to the expansion coefficient of the matrix as a critical property [7]. Avilés, reviewing the field in 2023, put the general position this way: when there is little filler the expansion of the polymer can outweigh the response of the filler itself, and as the network gets denser the balance moves the other way [8].

Anyone who sets out to make a thermometer from this material is left with three practical questions. What sign and what size of TCR should be expected? Over what interval does the resistance change in one direction only, so that a reading corresponds to a single temperature? And what function should be used for calibration? An experiment settles these for the one formulation that was tested. We wanted to know how much of the answer could be had in general, from a small physical model.

The model uses the two mechanisms that the literature keeps returning to, namely tunnelling helped by thermal fluctuations and the opening of junction gaps as the matrix expands. The glass transition enters as a step in the expansion coefficient. There are only a handful of parameters and each means something physical. We should say plainly that the paper contains no new measurements. Every curve in Section 4 is calculated. Their use is in sorting the features of the published data into those that follow from the two mechanisms and those that need some other explanation. Section 2 goes over the transport physics and Section 3 sets up the model. The results are in Section 4, and Section 5 takes up what they mean for a sensor.

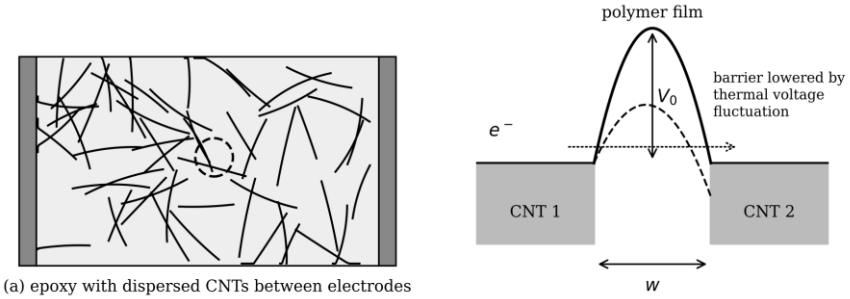
2 Theoretical Background

2.1 Percolation and the role of junctions

Above the percolation threshold φ_c, the d.c. conductivity of a random network of filler obeys $\sigma \propto (\varphi - \varphi_c)^t$, where φ is the volume fraction of filler and the exponent t is close to 2 in three dimensions. In nanotube epoxies the threshold is decided by processing at least as much as by the shape of the tubes. The tubes drift and flocculate while the resin is liquid, and whatever network exists at gelation is locked in.

Bauhofer and Kovacs gathered the thresholds published up to 2009 and found them scattered over three orders of magnitude, for materials that were nominally alike [2].

A power law of this kind counts conducting paths. It is silent on how charge gets from one tube to the next, and that step is where temperature comes in. Neighbouring tubes in a cured composite are kept apart by a film of polymer roughly a nanometre thick. Li, Thostenson and Chou calculated the tunnelling resistance of a contact like this and found it far larger than the resistance of the lengths of tube on each side [9]. Hu and co-workers came to the same view from simulations of the strain response [10]. It is therefore a fair approximation to treat the composite as a network of junctions and to take its temperature dependence from an average junction; the tubes add little. Figure 1 shows the picture we have in mind.



(a) epoxy with dispersed CNTs between electrodes

(b) energy diagram of one junction

Figure 1. (a) A percolated nanotube network in an epoxy matrix between two electrodes, shown schematically. One inter-tube junction is circled with a dashed line. (b) Energy diagram for that junction. The polymer film forms a barrier of height V_0 and width w, which thermal voltage fluctuations across the junction lower for brief intervals. Drawn by the author, following the model of Sheng [11], https://doi.org/10.1103/PhysRevB.21.2180.

2.2 Models of temperature dependent conduction

Three accounts of conduction in disordered materials are in general use. Thermal activation is the simplest. It gives $\sigma \propto \exp(-E_a/kT)$ and holds when carriers have to be lifted over a barrier of fixed height. It also requires the conductivity to vanish as the temperature goes to zero, and nanotube composites do not oblige: they still conduct at a few kelvin.

Mott's variable-range hopping is the second. Carriers hop between localised states, and $\sigma \propto \exp[-(T_M/T)^{1/(d+1)}]$, where d is the dimensionality [12]. The law describes many conducting polymers well, and some composites over restricted ranges of temperature. Its starting assumption is a continuous distribution of localised states. That is hard to accept for metallic tubes tens of micrometres long that are connected through a few thin gaps.

We use the third account, fluctuation-induced tunnelling (FIT). Sheng, Sichel and Gittleman proposed it for carbon black in poly(vinyl chloride) [13], and Sheng worked out the general theory two years later [11]. In this picture the conducting regions are large enough that charging energies can be ignored, while the junctions between them are small. A junction of area A and width w is then a capacitor with a tiny capacitance C, and thermal noise sets up a voltage of order $(kT/C)^{1/2}$ across it. The voltage fluctuates, and as it does it tilts and lowers the barrier (Figure 1(b)), which raises the probability of tunnelling. An average over the fluctuations leads to

$$\sigma(T) = \sigma_\infty \exp[-T_1 / (T + T_0)] \qquad (1)$$

T_1 is a measure of the energy an electron needs to pass over the barrier. The ratio T_1/T_0 sets the tunnelling probability when there are no fluctuations. For a barrier of height V_0,

$T_1 = 8\varepsilon_r\varepsilon_0 A V_0^2 / (e^2 k w)$, $T_0 = 2T_1 / (\pi\chi w)$, $\chi = (2mV_0)^{1/2} / \hbar$ (2)

Here ε_r is the relative permittivity of the polymer, ε_0 the permittivity of free space, e and m the charge and mass of the electron, k Boltzmann's constant and $\hbar$ the reduced Planck constant. Far below T_0, equation (1) goes to a constant, and what remains is plain elastic tunnelling. Far above T_0 it looks like activation over a barrier kT_1. Neitzert and co-workers read their nanotube epoxy data in terms of tunnelling between tubes [3], and the expression has a property that suits a sensor model: it is closed, so it can be solved for the temperature.

2.3 Thermal expansion of the matrix

Equation (1) assumes that the geometry of the junction never changes. In a real composite it does. A cured bisphenol-A epoxy expands linearly by roughly 50 to 70 × 10^{-6} K^{-1} while it is glassy, and by about three times as much above the glass transition temperature T_g. Along their axis nanotubes barely expand by comparison. So when the composite is heated the matrix carries the tubes away from each other. The probability of elastic tunnelling drops exponentially as the gap widens [14], which means that a small gain in w costs a disproportionate amount of resistance. This is the same mechanism that makes these composites respond to strain [10]. Here it opposes the FIT term.

The idea is an old one. Thermal expansion has long been accepted as the cause of the positive temperature coefficient in thermoplastics filled with carbon black, where crystallites melt and the volume jumps. An amorphous thermoset has nothing to melt. The step in expansion coefficient at T_g does a similar job, only more gently. Above T_g the chain segments are mobile, and the network may rearrange as well [4]. That change does not reverse on cooling, and we leave it out of the model.

3 Model and Method

We take the resistance of the composite to be the resistance of one representative junction times a geometric factor that is independent of temperature. For the junction we multiply the FIT factor of equation (1) by an elastic factor that follows the change in gap width, so that

$\ln[R(T)/R_\infty] = T_1/(T + T_0) + \beta[w(T) - w_0]$ (3)

β is the decay constant of the tunnelling probability with distance, and w_0 is the gap at the reference temperature T_{ref} = 300 K. We assume that the gap follows the matrix,

$w(T) = w_0[1 + \kappa \int \alpha_m(T')\, dT']$, the integral running from T_{ref} to T (4)

where α_m is the linear expansion coefficient of the epoxy and κ is the ratio of the local strain in the gap to the bulk thermal strain. If $\kappa = 1$ the gap deforms exactly as the bulk does. If κ is less than 1 the gap is constrained, which would be the case if the polymer inside it were a stiff interphase, or if the tubes were pinned by entanglement with their neighbours. If κ exceeds 1 the strain is concentrated in the gaps because the tubes themselves do not deform. Putting (4) into (3) and writing $g = \beta w_0 \kappa$, we get the two equations on which the rest of the paper depends,

$\ln[R(T)/R(300\ \mathrm{K})] = T_1/(T + T_0) - T_1/(300 + T_0) + g \int \alpha_m\, dT'$ (5)

$\mathrm{TCR} \equiv (1/R)\, dR/dT = -T_1/(T + T_0)^2 + g\alpha_m(T)$ (6)

The competition can be read straight off equation (6). Its first term is negative at every temperature and shrinks as the temperature rises. Its second term is positive at every temperature and jumps upward at T_g.

Should the two cancel inside the glassy interval or inside the rubbery one, the crossover falls at $T^{*} = [T_1/(g\alpha_m)]^{1/2} - T_0$.

Splitting equation (3) into two factors is an approximation (we come back to it in Section 5.4). Strictly speaking T_1 and T_0 depend on w through equation (2), and a consistent treatment would let both drift with temperature. We hold them fixed, for two reasons. First, the gap changes by much less than one percent over the range we study, so its direct effect on T_1 is small. Second, the barrier in the FIT expressions is an effective quantity that image forces have already lowered, whereas the sensitivity of the tunnelling current to distance is better captured by an empirical decay constant. Whatever is uncertain in β and in κ ends up inside the dimensionless group g.

Table 1 gives the values we used. The junction area is what one gets when two crossed tubes touch over about a nanometre. A gap of 1.5 nm is well inside the range where tunnelling is effective. We picked three barrier heights so that T_1 and T_0 would span what is found when equation (1) is fitted to measurements on nanotube composites; for T_1 that is from a few tens of kelvin to a few hundred. The expansion coefficients and the glass transition temperature are typical of a bisphenol-A epoxy cured with an amine. As a guide to the size of g, take $\beta = 10\ \mathrm{nm^{-1}}$, which is what the Simmons expression gives for a 1 eV barrier [14], and $w_0 = 1.5$ nm. Then $\beta w_0 = 15$, and $g = 5$, 10 and 20 correspond to κ of about 0.3, 0.7 and 1.3.

Table 1. Values of the parameters used in the calculations

Quantity	Value	Remark
Junction gap w_0	1.5 nm	Within tunnelling range
Junction area A	1 $\mathrm{nm^2}$	Crossed-tube contact
Relative permittivity ε_r	3.5	Cured epoxy, low frequency
Effective barrier V_0	0.05, 0.10, 0.20 eV	Cases A, B and C
Glassy expansion coefficient	$60 \times 10^{-6}\ \mathrm{K^{-1}}$	Below T_g
Rubbery expansion coefficient	$180 \times 10^{-6}\ \mathrm{K^{-1}}$	Above T_g
Glass transition T_g	400 K	Step change assumed
Gap-sensitivity parameter g	0, 5, 10, 20	$g = \beta w_0 \kappa$

Equations (2), (5) and (6) were evaluated numerically in Python on a temperature grid of 0.01 K. For the FIT-only runs ($g = 0$) the range was 80 to 400 K. The runs with expansion went from 250 to 450 K, which covers the temperatures of practical interest and reaches 50 K past T_g. To judge linearity we fitted a straight line to $R(T)$ between 273 and 373 K and took the largest deviation from it, expressed as a percentage of the resistance span over that interval.

4 Results

4.1 Tunnelling alone

Figure 2 shows the normalised resistance for the three barrier heights with expansion switched off; the numbers are in Table 2. Each curve falls steadily as the temperature rises, so the material is a negative temperature coefficient (NTC) resistor. The curves are convex and level out at the high end, which is what equation (1) demands.

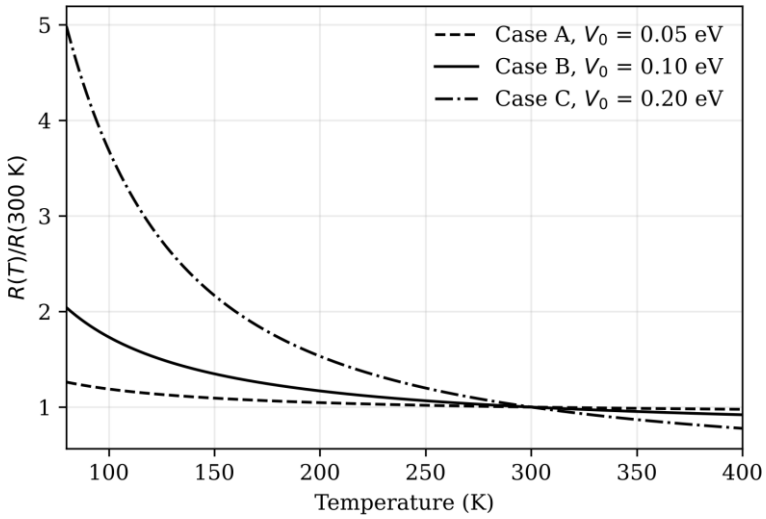


Figure 2. Resistance calculated for fluctuation-induced tunnelling alone (g = 0) and normalised to its value at 300 K. The three curves are for the effective barrier heights of cases A, B and C in Table 1.

How strong the effect is depends on the barrier height. T_1 goes as the square of the barrier, so taking V_0 from 0.05 to 0.20 eV multiplies T_1 by sixteen. The TCR at room temperature goes from −0.03 to −0.32% K^{-1}. Between 100 and 300 K the resistance in case A changes by 19%; in case C it changes by a factor of 3.7. Case B has T_1 = 120 K and T_0 = 31 K, which is near the middle of what fits to experimental data return, and we use it as the reference case from here on.

Table 2. Junction parameters and thermoresistive response calculated for tunnelling alone (g = 0)

Case	V_0 (eV)	T_1 (K)	T_0 (K)	R(100 K)/R(300 K)	TCR at 200 K	TCR at 300 K	TCR at 399 K
A	0.05	30	11	1.19	−0.067	−0.031	−0.018
B	0.10	120	31	1.73	−0.224	−0.109	−0.065
C	0.20	479	89	3.69	−0.574	−0.317	−0.201

TCR values are in % K^{-1}.

Two things in Table 2 matter to anyone designing a sensor. The first is that the TCR is far from constant. In case B it halves between 200 and 300 K and loses another 40% between 300 and 399 K, so the sensor becomes less sensitive as it warms up. The second is the size of the coefficient. Even in the best case, the room-temperature value is an order of magnitude smaller than that of a ceramic thermistor and somewhat smaller than that of platinum. On sensitivity alone, then, tunnelling does not make a good thermometer out of the composite. If the material has an advantage it has to be found somewhere else.

4.2 Effect of matrix expansion

The reference case with expansion included is plotted in Figure 3, and its TCR in Figure 4. Table 3 collects the results. Take g = 5 first. Through the glassy range the resistance still falls on heating, though more slowly than before, and the TCR at room temperature shrinks from −0.109 to −0.079% K^{-1}. At T_g the

expansion coefficient triples. The positive term in equation (6) then overtakes the negative one and the resistance starts to climb. The minimum of the curve lies exactly at the glass transition.

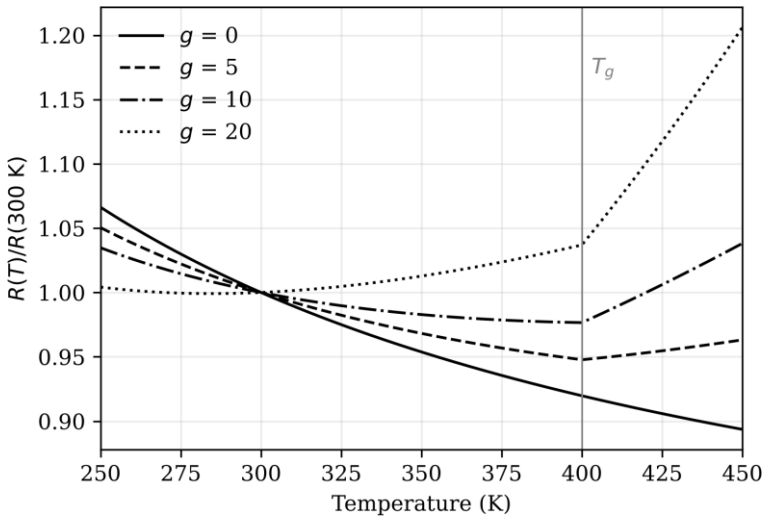


Figure 3. Resistance of case B, normalised to 300 K, calculated for four values of the gap-sensitivity parameter *g*. The vertical line is the glass transition temperature assumed for the epoxy.

For $g = 10$ the picture is the same, only stronger. The TCR in the glass is halved once more, and above T_g the rise is steep enough that by 450 K the resistance is higher than it was at 300 K. The minimum is at T_g again. There is a simple reason for this pinning. For both values of g, the crossover temperature T^* worked out with the glassy expansion coefficient comes out above 400 K, while T^* worked out with the rubbery coefficient comes out below 400 K. So the TCR is negative throughout the glass and positive throughout the rubber, and the only place where the sign can change is the step. With the parameters of case B this is true for any g from about 3.6 to 10.7, which is a threefold range. On this model, a resistance minimum at the glass transition is what a nanotube epoxy should normally show, and anything else is the exception.

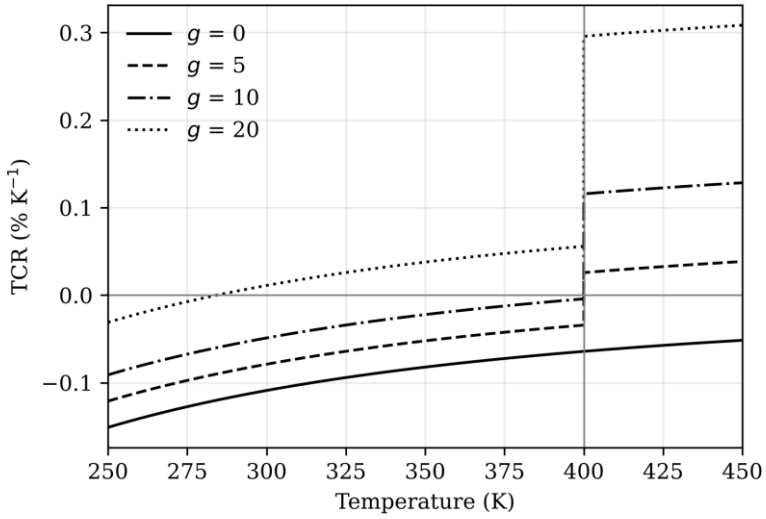


Figure 4. Temperature coefficient of resistance of case B for the same four values of *g*. The step at 400 K comes from the change in expansion coefficient at the glass transition.

At g = 20 the behaviour is of a different kind. Expansion is now strong enough to cancel tunnelling inside the glassy range, and the minimum comes down to 284 K. Near room temperature the resistance scarcely depends on temperature: it varies by under 0.1% between 284 and 300 K, and the TCR at 300 K is +0.011% K^{-1}. As a thermometer such a material would be poor in exactly the range where thermometers are most wanted. It could, on the other hand, serve as a temperature-compensated strain gauge.

Table 3. Response of case B calculated with matrix expansion included

g	TCR at 300 K	TCR at 420 K	Temperature of minimum (K)	R(450 K)/R(300 K)
0	−0.109	−0.059	none below 450	0.894
5	−0.079	+0.031	400	0.963
10	−0.049	+0.121	400	1.038
20	+0.011	+0.301	284	1.206

TCR values are in % K^{-1}.

Including expansion makes the response less linear. From 273 to 373 K the FIT-only curve departs from a straight line by at most 6.1% of span. The figure is 8.1% for g = 5 and 13.8% for g = 10. At first sight this is odd, because inside the glass the expansion term is itself linear in temperature. What happens is that it takes a linear part away from the response and does nothing to the curvature of the FIT term. The span gets smaller while the curvature stays as it was, and so the nonlinearity relative to span grows.

5 Discussion

5.1 Comparison with published observations

The main qualitative findings in the literature come out of the model without any special assumptions. Neitzert and co-workers saw a negative coefficient well below T_g in a 0.5 wt% composite [3]; that is small or moderate g. Lasater and Thostenson [4] saw a coefficient that changes sign with temperature, and so did Dai and co-workers when they cycled specimens between 25 and 145 °C [6]; that is the minimum in Figure 3. The nearly flat response below T_g that Jafarypouria and Abaimov report for a fully cured composite at about 1 wt% [7] looks like our g = 20 curve, where the two terms cancel close to room temperature. And the wholly positive coefficient of the expansion-only model of Cen-Puc and colleagues [5] is what remains when the tunnelling term is dropped, because the second term of equation (6) is positive at all temperatures. Their model and the FIT description are thus two limits of one expression.

The model also hints at why loading matters. Close to the percolation threshold, the current runs along a few paths that pass through the widest gaps. Those gaps have large w and therefore, by equation (2), small T_1, and the tunnelling term is weak. The near-zero negative TCR that Lasater and Thostenson found close to threshold [4] agrees with this reading, though we cannot exclude an accidental cancellation like the one at g = 20. At higher loadings the gaps are narrower and there are more of them, so both terms grow. Which term wins then turns on κ, that is, on how firmly the denser network holds the matrix in the gaps. The remark by Avilés that polymer expansion tends to dominate at low filler content [8] was made about a

class of materials much wider than epoxy. Our model would give the same result for matrices with a high expansion coefficient.

Hysteresis is beyond the model. Experiments often show the first heating run differing from later ones, and some show the resistance creeping at constant temperature above T_g. These effects are generally put down to physical ageing, completion of cure and the network rearrangement mentioned in Section 2.3. A reversible model such as ours describes a specimen that has been cycled thermally until its response repeats.

5.2 Calibration

Thermistors are normally calibrated with the Steinhart-Hart equation, a polynomial in ln R with three constants [15]. Equation (1) gives the nanotube composite a calibration function with the same number of constants, and with a physical basis as well,

$$T = T_1 / (\ln R - \ln R_\infty) - T_0 \qquad (7)$$

Three fixed points are enough to find R_∞, T_1 and T_0. Where expansion is appreciable, equation (5) brings in a term linear in temperature within the glassy range, and with it a fourth constant, $g\alpha_m$. The function can no longer be inverted in closed form. It is still monotonic below the crossover, though, and a numerical inversion or a look-up table will do. Our suggestion is that authors who report thermoresistive data should fit equation (5) and quote all four constants. One averaged TCR does not carry enough information: in Table 2 the coefficient changes by a factor of three over a range that papers routinely sum up in a single number.

5.3 Sensitivity, resolution and range

Table 4 sets the calculated coefficients beside those of the two standard resistive sensors. Of the three, the composite is the least sensitive. Suppose the resistance is measured in the ordinary way, to one part in 10^4. The temperature resolution is that figure divided by the TCR, which comes to about 0.13 K for case B with $g = 5$ and about 0.03 K for case C without expansion. That is good enough for cure monitoring and for thermal mapping of structures. It is not good enough for laboratory thermometry.

Table 4. Resistive temperature sensors compared

Sensor	TCR near 300 K (% K^{-1})	Typical upper limit	Remarks
Platinum resistor (Pt100)	+0.385	Above 600 °C	Nearly linear, stable, discrete component
NTC ceramic thermistor [15]	about −3 to −5	150 to 300 °C	Strongly nonlinear, high sensitivity, brittle
CNT/epoxy, this work, tunnelling alone	−0.03 to −0.32	Below T_g	Calculated, cases A to C

Sensor	TCR near 300 K (% K^{-1})	Typical upper limit	Remarks
CNT/epoxy, this work, with expansion	−0.08 to +0.01	Below the resistance minimum	Calculated, case B with g = 5 to 20

The resistance minimum sets the upper end of the useful range. Past it, two temperatures share one resistance and the reading cannot be trusted. For moderate g the limit is T_g, and in common epoxies T_g is anywhere from about 60 to 200 °C depending on the hardener and the cure schedule. A high-T_g formulation is therefore the better choice on electrical grounds, quite apart from the mechanical ones. For large g the limit can come down close to room temperature, and a formulation like that should simply be rejected.

Because g decides the outcome, it is worth asking how to make it smaller. By its definition g is small when the gaps are narrow, or when the matrix in the gaps is constrained. A higher loading, better dispersion, and a post-cure that raises the crosslink density all push that way. Choosing a matrix with a lower expansion coefficient reduces the product $g\alpha_m$ directly. Sensitivity can also be approached through the barrier height. T_1 rises as the square of V_0 (Table 2) and the TCR rises with it. Chemical functionalisation of the tubes alters the barrier at the interface, but it usually changes the conductivity of the composite too. Whether it can raise the TCR without costing too much conductivity is a question that only experiment will settle.

The most serious practical difficulty is cross-sensitivity to strain. The mechanism that gives g its importance also gives the composite a gauge factor of order 10 [10]. A mechanical strain of 10^{-4} then shifts the resistance by 0.1%, and with a TCR of −0.1% K^{-1} the instrument reads that as an error of 1 K. A sensor bonded to a structure whose expansion coefficient differs from its own will pick up a thermal mismatch strain of this size for every few kelvin of temperature change. There are two remedies. The sensing element can be mounted so that the substrate puts no load on it, or it can be paired with a reference element that does not respond to strain. Self-heating by the measuring current has to be kept small too. The composite conducts heat poorly, and the very same material has been used on purpose as a heater [3].

5.4 Limitations of the model

The simplifications in the model should be kept in view. One representative junction stands in for a whole distribution of gaps and areas. In a real network the current redistributes when the temperature changes, so the effective junction at 100 K is not the effective junction at 400 K. The factorisation in equation (3) treats fluctuation-assisted tunnelling and elastic tunnelling as independent. That is reasonable when the gap changes little, but it has not been derived rigorously. We represent the glass transition as a step, whereas dilatometry shows it spread over 10 to 20 K; the sharp minima of Figure 3 would be rounded in a real specimen. We neglect network rearrangement above T_g, moisture uptake, and the temperature dependence of the resistance of the tubes themselves. Last, the junction parameters in Table 1 are plausible values and were not measured. Different combinations of A, w and V_0 lead to the same T_1 and T_0, and no fit to resistance data can tell them apart.

None of this touches the structure of equation (6), and our qualitative conclusions rest on that structure alone. The numbers in Tables 2 and 3 are illustrations for the stated parameters and should not be taken as predictions for any particular material.

6 Conclusions

We have studied how the resistance of nanotube epoxy composites depends on temperature, using a model in which two terms compete. One is fluctuation-induced tunnelling at the junctions between tubes, and the other is the widening of those junctions as the matrix expands.

Tunnelling by itself produces a negative temperature coefficient. For effective barriers of 0.05 to 0.20 eV its magnitude at 300 K lies between 0.03 and 0.32% K^{-1}; it grows as the square of the barrier height and gets steadily weaker as the temperature rises. Expansion of the matrix works against it, and a single dimensionless number g controls how strongly. (g is the product of the tunnelling decay constant, the gap width and the ratio of gap strain to bulk strain.) In the reference case, with g roughly between 4 and 11, the resistance passes through a minimum that is pinned at the glass transition temperature. We think this is the origin of the TCR sign reversals seen in several experimental studies. When g is larger the minimum moves down into the glassy range. It can end up near room temperature, and the composite then hardly responds to temperature at all.

Judged as a thermometer the composite is less sensitive than platinum and much less sensitive than a thermistor. What speaks for it is that it can be cast or printed in place and built into a structure made of the same resin. Below T_g a resolution of the order of 0.1 K looks attainable, so long as the element is kept free of mechanical strain. For calibration, and for reporting data, we recommend the four-constant form of equation (5).

What is needed next is an experiment. Resistance and dilatometric strain should be measured on the same specimens, through T_g, at several loadings. Data of that kind would give g directly, and they would show whether a single representative junction is an adequate description of the network.

REFERENCES:

[1] S. Iijima, Helical microtubules of graphitic carbon, *Nature* 354 (1991) 56-58.

[2] W. Bauhofer, J.Z. Kovacs, A review and analysis of electrical percolation in carbon nanotube polymer composites, *Compos. Sci. Technol.* 69 (2009) 1486-1498. https://doi.org/10.1016/j.compscitech.2008.06.018

[3] H.C. Neitzert, L. Vertuccio, A. Sorrentino, Epoxy/MWCNT composite as temperature sensor and electrical heating element, *IEEE Trans. Nanotechnol.* 10 (2011) 688-693.

[4] K.L. Lasater, E.T. Thostenson, In situ thermoresistive characterization of multifunctional composites of carbon nanotubes, *Polymer* 53 (2012) 5367-5374. https://doi.org/10.1016/j.polymer.2012.09.022

[5] M. Cen-Puc, A.I. Oliva-Avilés, F. Avilés, Thermoresistive mechanisms of carbon nanotube/polymer composites, *Physica E* 95 (2018) 41-50. https://doi.org/10.1016/j.physe.2017.09.001

[6] H. Dai, E.T. Thostenson, T. Schumacher, Comparative study of the thermoresistive behavior of carbon nanotube-based nanocomposites and multiscale hybrid composites, *Compos. Part B* 222 (2021) 109068. https://doi.org/10.1016/j.compositesb.2021.109068

[7] M. Jafarypouria, S.G. Abaimov, Near-zero temperature coefficient of resistance for a single-walled carbon nanotube polymer nanocomposite, arXiv preprint arXiv:2503.13736 (2025). https://arxiv.org/abs/2503.13736

[8] F. Avilés, Thermoresistivity of carbon nanostructures and their polymeric nanocomposites, *Adv. Mater. Interfaces* 10 (2023) 2300218. https://doi.org/10.1002/admi.202300218
[9] C. Li, E.T. Thostenson, T.-W. Chou, Dominant role of tunneling resistance in the electrical conductivity of carbon nanotube-based composites, *Appl. Phys. Lett.* 91 (2007) 223114.
[10] N. Hu, Y. Karube, C. Yan, Z. Masuda, H. Fukunaga, Tunneling effect in a polymer/carbon nanotube nanocomposite strain sensor, *Acta Mater.* 56 (2008) 2929-2936. https://doi.org/10.1016/j.actamat.2008.02.030
[11] P. Sheng, Fluctuation-induced tunneling conduction in disordered materials, *Phys. Rev. B* 21 (1980) 2180-2195. https://doi.org/10.1103/PhysRevB.21.2180
[12] N.F. Mott, Conduction in non-crystalline materials, *Philos. Mag.* 19 (1969) 835-852.
[13] P. Sheng, E.K. Sichel, J.I. Gittleman, Fluctuation-induced tunneling conduction in carbon-polyvinylchloride composites, *Phys. Rev. Lett.* 40 (1978) 1197-1200.
[14] J.G. Simmons, Generalized formula for the electric tunnel effect between similar electrodes separated by a thin insulating film, *J. Appl. Phys.* 34 (1963) 1793-1803.
[15] J.S. Steinhart, S.R. Hart, Calibration curves for thermistors, *Deep-Sea Res.* 15 (1968) 497-503.