

Supplementary data

Double-segregated MWNT/silicone Composites with Large Electrical to Thermal Conductivity Ratio via In-situ Silicone Emulsion Polymerization

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Thermal conductivity of MWNT/silicone composites having microvoids

In analyzing the thermal transport behaviour in heterogeneous media, various effective medium approaches like the Maxwell-Garnett approximation have been used to determine effective thermal conductivities of different composite structures [S1,S2]. The validity of the conventional effective medium approaches was proved for carbon nanotube composites by C. W. Nan et al. [S3]. Meanwhile, large interface thermal resistance (Kapitza resistance) of carbon nanotube was determined by the Cahill and Koblinski group as $\sim 8.3 \times 10^{-8} \text{ m}^2\text{-K/W}$ [S4]. Their finding explained that experimentally-measured thermal conductivity of CNT composite was much lower than the value estimated from the intrinsic thermal conductivity of the nanotubes and their volume fraction. After the observation, thermal conductivity of CNT composites was re-assessed by combining the Kapitza resistance with the effective medium approach [S5]. The resultant effective thermal conductivity, K_e , of the composite with CNTs randomly dispersed in a matrix can be described as

$$\frac{K_e}{K_m} = \frac{3+f(\beta_x+\beta_z)}{3-f\beta_x} \quad (\text{E1})$$

with

$$\beta_x = \frac{2(K_{11}-K_m)}{K_{11}+K_m}, \quad \beta_z = \frac{K_{33}}{K_m} - 1 \quad (\text{E2})$$

where f is the volume fraction of the nanotubes; K_{11} and K_{33} are the equivalent thermal conductivities along transverse and longitudinal axes of a composite unit cell, i.e., a nanotube coated with a very thin interfacial thermal barrier layer, and can be expressed as [S4]

$$K_{11} = \frac{K_c}{1 + \frac{2a_k K_c}{d K_m}}, \quad K_{33} = \frac{K_c}{1 + \frac{2a_k K_c}{l K_m}} \quad (\text{E3})$$

where d and l ($p=l/d$) are the diameter and length of the nanotubes, respectively; and a_K is a so-called Kapitza radius defined by $a_K=R_K \cdot K_m$. By taking $R_K=8 \times 10^{-8} \text{ m}^2 \cdot \text{K}/\text{W}$ and $K_m=0.2 \text{ W}/\text{m} \cdot \text{K}$ for the silicone rubber, The Kapitza radius results in $1.6 \times 10^{-8} \text{ m}$. Effective thermal conductivity of MWNT/B-silicone composites is deduced from the parameters suggested in equation (E1)-(E3). We took $K_e=3000 \text{ W}/\text{m} \cdot \text{K}$ and $d=10 \text{ nm}$ for the calculation. The thermal conductivity increased with increasing MWNT contents and with increasing MWNT aspect ratio.

With the inclusion of internal voids in MWNT/E-silicone composites, thermal conductivity was even lowered, compared to that of MWNT/B-silicone composites. Theoretical values of MWNT/E-silicone composites having internal voids were calculated with Maxwell-Eucken (equation E4) and Landauer's relation (equation E5) as below [S6,S7].

$$K = \frac{\frac{1}{4} [K_p(3P_v - 1) + K_e(2 - 3P_v)]}{+ \{ [K_p(3P_v - 1) + K_e(2 - 3P_v)]^2 + 8K_eK_p \}^{1/2}} \quad (\text{E4})$$

$$K = K_e \frac{K_p + 2K_e + 2P_v(K_p - K_e)}{K_p + 2K_e - P_v(K_p - K_e)} \quad (\text{E5})$$

where K_e and K_p represent thermal conductivities of the composite and porous medium ($0.02 \text{ W}/\text{m} \cdot \text{K}$ for air). And P_v represents volume fraction of internal void in the composite. If thermal conductivity of the composites having microvoids is compared with that of the composites having no void, theoretical values calculated from the equations are still in the same order of magnitude. On the other hand, experimentally-measured values show bigger difference. When microvoids were introduced into the composites, thermal conductivity was one order of magnitude lowered.

References

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Heating performance of MWNT/silicone composites

Electrical power applied to the specimens can be described as equation (F1).

$$P = \frac{V^2}{R} = \frac{\sigma \cdot A \cdot V^2}{L} \quad (F1)$$

where σ represents electrical conductivity and A and L represents cross-sectional area and length of the conductor. The heating element works by converting electrical input into thermal energy. Electrical power input can be expressed as equation (F1). With a specific voltage applied, electrical power can be elevated by decreasing resistance of conducting materials. That is, higher electrical conductivity would be more profitable to exert maximum power. That is, to reach a same level of conductivity, MWNT/E-silicone composite is more advantageous than MWNT/B-silicone.

To operate resistive heater, electrical energy input must be converted into thermal energy. The energy balance can be expressed as equation (F2).

$$E = Pt = \frac{V^2 t}{R} = mC\Delta T \quad (F2)$$

where C and ΔT represent heat capacity and temperature difference, respectively. Heat capacities of air (300K), silicone and nanotube were set at 1.005, 1.46 and 0.7 J/g·K. Effective heat capacities of the composites can be calculated with equation (F3) and (F4).

$$C_e = (v_v \rho_v C_v + v_M \rho_M C_M + v_s \rho_s C_s) / \rho_e \quad (F3)$$

with

$$\rho_e = (v_v \rho_v + v_M \rho_M + v_s \rho_s) \quad (F4)$$

where v and ρ represent volume fraction and density. Subscript v , M , s and e represent void, MWNT,

silicone and composite, respectively. The calculated heat capacities were 1.33, 1.32 and 1.28 J/g·K for the composites having 0, 10 and 30 vol.% of voids inside.

Microstructure of thick MWNT/E-silicone composite coating

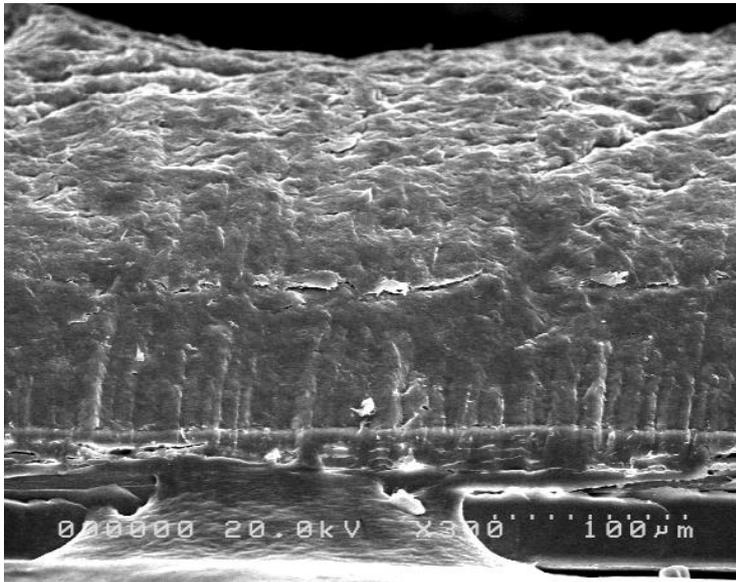


Fig. S1. The MWNT/E-silicone composite having a thickness of $\sim 220\mu\text{m}$. Fabrication of very thick film was achieved through layer by layer deposition process where pre-coated layer had been half-cured instantly before the overcoating layer arrived on it.