Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Calculation of thermal stress and stress relaxation of superhydrophobic MWNT–silicone composite

The changing thermal stresses in the MWNT–silicone composite coatings on Si (100) substrates were calculated and compared with those measured using the laser curvature method. The elastic moduli and coefficients of thermal expansion (CTEs) were extracted from randomly oriented isotropic models. Here, theoretical calculations of the elastic modulus, CTE, and thermal stress were conducted, assuming that all the composite coatings, regardless of MWNT content, had completely filled microstructures without any pores. First, the elastic modulus of the composite (E_c) can be obtained from Equation S1 [1]:

$$E_c = \frac{3}{8}E_{11} + \frac{5}{8}E_{22}$$

$$E_{11} = \frac{1 + 2(l_{NT}/d_{NT})\eta_L V_{NT}}{1 - \eta_L V_{NT}} E_m$$

$$E_{22} = \frac{1 + 2\eta_T V_{NT}}{1 - \eta_T V_{NT}} E_m$$

$$\eta_L = \frac{E_{NT}/E_m - 1}{E_{NT}/E_m + 2(l_{NT}/d_{NT})}$$

$$\eta_T = \frac{E_{NT}/E_m - 1}{E_{NT}/E_m + 2}$$

Here, *l*, *d*, *V,* and *E* represent the length, diameter, volume fraction, and elastic modulus, respectively. The subscripts c, NT, and m represent composite, nanotube, and matrix. The specific values and their references are summarized in Table S1.

Table S1. Material properties of MWNT and silicone (Sylgard 184) used for this study.

MWNT					silicone [5]		
Length (l, μm)	Diameter (d, nm)	Modulus [2] (E,GPa)	CTE [3] (α,ppm ℃$^{-1}$)	Poisson's ratio [4] (ν)	Modulus (E, GPa)	CTE (α,ppm ℃$^{-1}$)	Poisson's ratio (ν)
12	12	900	7	0.27	0.0018	310	0.5

Next, the coefficient of thermal expansion of the composite (α_c) can also be calculated from Equation S2 [6,7]:

$$\alpha_c = \frac{\alpha_{11} + \alpha_{22}}{2} + \frac{(E_{11} - E_{22})(\alpha_{11} - \alpha_{22})}{2[E_{11} + (1 + 2\nu_{12})E_{22}]}$$

where

$$\alpha_{11} = \frac{\alpha_{NT}E_{NT}V_{NT} + \alpha_m E_m(1 - V_{NT})}{E_{NT}V_{NT} + E_m(1 - V_{NT})}$$

$$\alpha_{22} = (1 + \nu_{NT})\alpha_{NT}V_{NT} + (1 + \nu_m)\alpha_m(1 - V_{NT}) - \nu_{12}\alpha_{11}$$

$$\nu_{12} = \nu_{NT}V_{NT} + \nu_m V_m$$

Here, α and ν represent the CTE and Poisson's ratio, respectively. The elastic moduli and CTE values calculated from Equations S1 and S2 are presented in Figure S1. The elastic modulus of the composite increased as the MWNT content increased, while the CTEs showed the opposite trend.

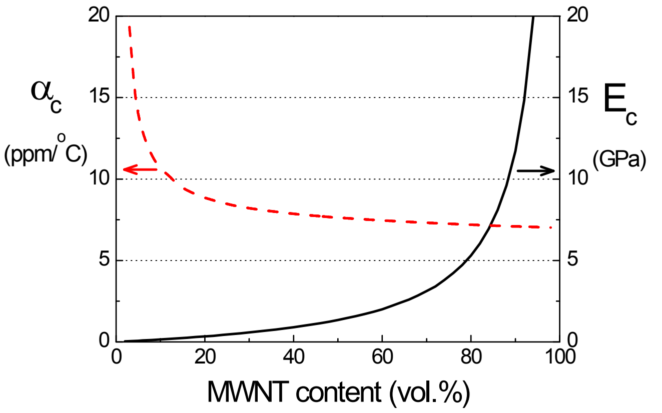

Figure S1. Elastic modulus (E_c) and coefficient of thermal expansion (α_c) of the MWNT–silicone composite calculated using Equations S1 and S2.

The thermal stress (σ_{th}) that evolved from the CTE mismatch of the thin film–substrate is described by Equation S3 [8]:

$$\sigma_{th} = -(\frac{E}{1-\nu})_f(\alpha_f - \alpha_s)\Delta T \quad \text{(S3)}$$

Here, the subscripts f and s represent film and substrate, respectively. The CTE value for Si (100) was set at 2.6 ppm °C^{-1}. For the MWNT–silicone composite film, the thermal stress ratios with respect to the film with specific filler content can be obtained from Equation S4, assuming that the Poisson's ratios (ν) were the same for the films with MWNT content of 5–40 vol%.

$$\frac{\sigma_2}{\sigma_1} = \frac{E_{f2}}{E_{f1}}(\frac{\alpha_{f2} - \alpha_s}{\alpha_{f1} - \alpha_s}) \quad \text{(S4)}$$

The relative stress ratios are shown in Table S2 (see also Figure 5 in the paper), with the stress value of the 5% MWNT–silicone composite film set as the reference: σ_{th} (5 vol%) = 1. Stress relaxation, induced from plastic deformation of the silicone matrix or defects in the composite film, was ignored for simplicity. The theoretical thermal stress increased rapidly as the MWNT content increased, suggesting that the elastic modulus is more important than CTE for stress evolution of the composite films.

Table S2. Stress relaxation estimated from the difference between theoretical calculation and experimental measurement.

MWNT content (vol%)	5	10	20	30
σ_{th} ratio (Equation S4)	1.0	1.46	2.58	3.94
$\Delta\sigma/\Delta T$ (KPa℃$^{-1}$) (from Figure 4)	-3.84	-4.48	-5.16	-2.43
$\Delta\sigma/\Delta T$ ratio	1.0	1.17	1.34	0.63
stress relaxation (%)			48	84

References

[1] D. Qian, E. C. Dickey, R. Andrews, T. Rantell, *Appl. Phys. Lett.* **2000**, *76*, 2868.
[2] K. M. Liew, X. Q. He, C. H. Wong, *Acta Mater.* **2004**, *52*, 2521.
[3] F. Y. Wu, H. M. Cheng, *J. Phys. D: Appl. Phys.* **2005**, *38*, 4302.
[4] J. P. Lu, *Phys. Rev. Lett.* **1997**, *79*, 1297.
[5] *Information about Dow Corning brand Silicone encapsulants*. Form No. 10-898I-01.

[6] H. Guo, T. V. Sreekumar, T. Liu, M. Minus, S. Kumar, *Polymer* **2005**, *46*, 3001.
[7] P. K. Mallick, *Composites Engineering Handbook*, Marcel Dekker, New York, USA **1997**.
[8] D. S. Gardner, P. A. Flinn, *IEEE Trans. Electron Devices* **1988**, *35*, 2160.

Volume fraction of the constituents of MWNT-silicone composite films

weight					volume				
CNT	184A	184B	Triton X	total WT	CNT	184A	184B	Triton X	total VOL
9.25	90.27	9.03	0.46	109.01	5.00	85.97	8.60	0.43	100.00
18.50	85.08	8.51	0.93	113.02	10.00	81.03	8.10	0.86	100.00
37.00	74.71	7.47	1.85	121.03	20.00	71.16	7.12	1.73	100.00
55.50	64.34	6.43	2.78	129.05	30.00	61.28	6.13	2.59	100.00
74.00	53.97	5.40	3.70	137.07	40.00	51.40	5.14	3.46	100.00
DENSITY：CNT 1.85g/cc, sylgard 184 1.05g/cc, triton X 1.07g/cc									

SEM micrographs of MWNT-silicone composite films on Al & Si substrate

Al substrate Si substrate