Structure-induced Variation of Thermal Conductivity in Epoxy Resin Fibers

Xiaoliang Zeng,[a, ‡] Yucheng Xiong,[b, ‡] Qiang Fu, [b] Rong Sun, [a,*] Jianbin Xu,[c] Dongyan Xu, [b,*] and Ching-Ping Wong [c, d]

[a]Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China. E-mail: rong.sun@siat.ac.cn

[b]Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong Special Administrative Region, China. E-mail: dyxu@mae.cuhk.edu.hk

[c]Department of Electronic Engineering, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong Special Administrative Region, China

[d]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

‡ Xiaoliang Zeng and Yucheng Xiong contributed equally to this work.

1

1. Raw materials

A liquid crystal epoxy resin, 4, 4'− bis (4–hydroxybenzoyloxy) −3, 3'5, 5'− tetramethyl biphenyl, was purchased from Gansu Research Institute of Chemical Industry, China. 4, 4'– diaminodiphenylsulphone and triphenylphosphine, used as the curing agent and catalysts, respectively, were purchased from Sigma-Aldrich. Other materials and reagents were purchased from Sinopharm Chemical Reagent Co., Ltd, China. All chemicals were used as received.

2. Preparation of epoxy resin fibers

Solutions of epoxy resins with the concentration from 60 wt% to 70 wt% were prepared in 2-butanone by stirring the solution at 30 °C for 4 hr. The clear and homogeneous solutions were then transferred to a 5.0 mL syringe and used for the electrospinning process. The needle-to-collector distance, electrical voltage, and volumetric flow rate were fixed at 20 cm, 15 kV, and 0.02 mL/min, respectively. Relative humidity was around 70–80%. The electrospun epoxy resin fibers were deposited onto a stationary collector. The collected epoxy resin fibers were dried at 50 °C for 12 hr to remove the residual solvent. Finally, the dried fibers were cured by a programmed heating process within the temperature range of 150–220 °C for 2 hr.

3. Characterization

Scanning electron microscopy characterization was performed with a FEI Nova Nano SEM 450 field emission electron microscope. The specific heat of epoxy resin fibers was measured by differential scanning calorimetry, according to ISO 1135-4:2005 Standard. The specific heat measurements were performed on a TA Q2000 differential scanning calorimeter at a heating rate of 10 °C min^{-1}. Polarized Fourier-transform infrared (FTIR) spectra were obtained in transmission mode with pure KBr as the background with a Bruker Vertex 70 spectrometer. The alignment function was calculated according to our previous report.[S1] The thermal conductivity of the bulk epoxy resins was determined by using a LW-9389 TIM Resistance and Conductivity Measurement apparatus (Long Win Science & Technology, Taiwan), which was built according to the ASTM D-5470-06 standard.

4. Thermal conductivity measurement principle of epoxy resin fibers

The thermal conductivity of the single epoxy resin fiber was measured using a well-established suspended micro-device method over a wide temperature range.[S2] The micro-device consists of two suspended 25 μm × 15 μm silicon nitride membranes separated by several microns. A 50 nm thick platinum coil and a platinum electrode (3 μm wide) were patterned on each membrane. Each coil was electrically connected to four contact pads via metal lines on the suspended beams, enabling the four-probe measurement of the electrical resistance of the platinum coil. The platinum coil serves as a heater to increase the temperature of the suspended membrane (heat source), as well as a resistance thermometer to measure the temperature of each suspended membrane (heat source or heat sink). A single epoxy resin fiber was placed bridging two membranes by using a micromanipulator. The thermal conductivity measurements were performed in a vacuum chamber with the pressure lower than 10^{-5} Torr.

During a measurement, one membrane (heat source) was heated up by passing a direct current (I) through the platinum coil. The Joule heat generated in the platinum coil (Q_h) and the counterpart generated in one supporting beam (Q_b) can be calculated by

$$Q_h = I^2 R_h , \tag{S1}$$

and

$$Q_b = I^2 R_b . \tag{S2}$$

The temperature of the heating membrane is raised to T_h. Part of the generated heat (Q_2) was conducted through the epoxy resin fiber to the other membrane (heat sink), raising its temperature to T_s. Q_2 can be determined by solving the equivalent thermal circuit as,

$$Q_2 = G_b(T_s - T_0) = G_s(T_h - T_s) , \tag{S3}$$

where G_s and G_b are the thermal conductance of the fiber and supporting beams, respectively. Considering the energy conservation of the whole micro-device, one can obtain

$$G_b = \frac{Q_h + Q_b}{\Delta T_h + \Delta T_s}, \tag{S4}$$

and

$$G_s = G_b \frac{\Delta T_s}{\Delta T_h - \Delta T_s}. \tag{S5}$$

A small alternating current (ac) was applied to the platinum coil on the heating membrane to measure the coil resistance using a four-probe method and the temperature rise of the heating membrane can be calculated from the change of the coil resistance,

$$\Delta T_h(I) = \frac{\Delta R_h(I)}{\frac{dR_h(I=0)}{dT}}, \text{ where } \Delta R_h(I) \equiv R_h(I) - R_h(I=0). \tag{S6}$$

An ultra-sensitive measurement technique based on the Wheatstone bridge was employed to determine the temperature rise of the sensing membrane as shown in Fig. 2 in the main manuscript.[S3] In this method, a reference device without the epoxy resin fiber is used to cancel the measurement noise at the sensing side by the common mode rejection. On the other hand, the background conductance between the heating membrane and the sensing membrane also contributes to the measured total thermal conductance, which results in an overestimation of thermal conductivity of the nanofiber. To eliminate the contribution of the background conductance, an identical heating power was applied to the heating coil on both the measurement device (with the fiber) and the reference device (without the fiber); then thermal conductance of the fiber can be determined from the offset voltage of the Wheatstone bridge.

To do so, a small ac voltage (v_s) is applied to the sensing circuit. Before the measurement, the Wheatstone bridge at the sensing side is balanced by tuning two variable resistances R_2 and R_3. During the measurement, the offset voltage of the Wheatstone bridge (v_g) is detected by a lock-in amplifier, which can be expressed as

$$v_g = v_A - v_B = \frac{R_2}{R_s + R_2} v_s - \frac{R_3}{R_1 + R_3} v_s. \tag{S7}$$

Then, the sensing resistance (R_s) can be derived by

4

$$R_s = \frac{R_2}{(\frac{v_g}{v_s} + \frac{R_3}{R_1 + R_3})} - R_2 \,. \tag{S8}$$

It is worth noting that the measured sensing resistance is the sum of the resistance of the sensing coil (R_{sc}) and the resistance of two supporting beams ($2R_b$),

$$R_s = R_{sc} + 2R_b \,. \tag{S9}$$

The temperature of the sensing coil can be considered to be uniform. However, the temperature of the supporting beam varies linearly from T_s to T_0. Therefore, the change in the sensing resistance is given by

$$\Delta R_s = 2R_b[\frac{1}{R_s}\frac{dR_s}{dT}(\frac{T_s - T_0}{2})] + R_{sc}\frac{1}{R_s}\frac{dR_s}{dT}(T_s - T_0) \,. \tag{S10}$$

Thus, temperature rise of the sensing membrane can be determined by

$$\Delta T_s = T_s - T_0 = \frac{2R_b + R_{sc}}{R_b + R_{sc}} \frac{\Delta R_s}{\frac{dR_s}{dT}} \,. \tag{S11}$$

Once ΔT_h and ΔT_s are determined, G_s can be calculated by using Eq. (S4) and (S5). The total thermal resistance of the epoxy resin fiber (R_{tot}) is derived by taking the reciprocal of G_s.
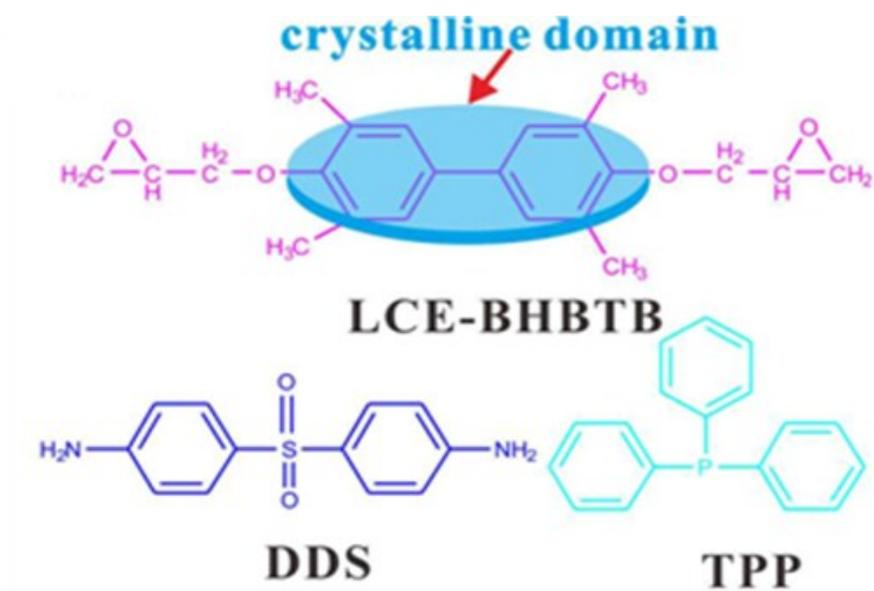
Fig. S1. Chemical structures of the epoxy resin monomer (LEC-BHBTB), the curing agent (DDS), and

the catalyst (TPP).
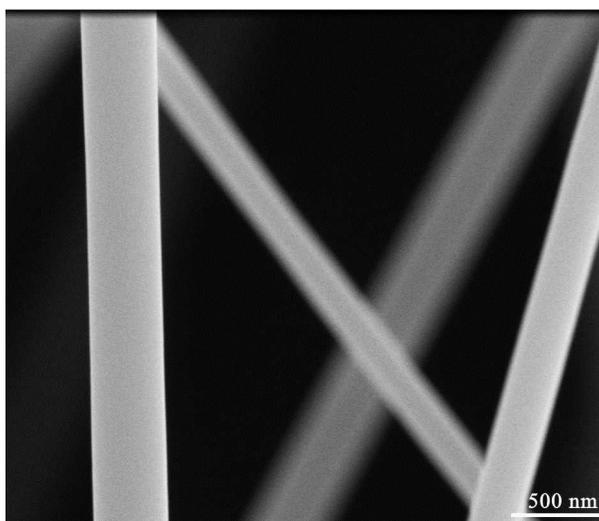
Fig. S2. SEM image of the epoxy resin fibers with the diameter of 394±20 nm.

References

S1. X. Zeng, L. Ye, K. Guo, R. Sun, J. Xu and C.-P. Wong, *Adv. Electron. Mater.*, 2016, 1500485.

S2. L. Shi, D. Li, C. Yu, W. Jang, D. Kim, Z. Yao, P. Kim and A. Majumdar, *J. Heat Transfer*, 2003, **125**, 881-888.

S3. M. C. Wingert, Z. C. Y. Chen, S. Kwon, J. Xiang and R. Chen, *Rev. Sci. Instrum.,* 2012, **83**, 024901.