Enhancement of Thermal Conductivity of Polyvinyl Alcohol Membrane Using Nano-fiber

Xiandong Chen[1,2#], Meng An[1,2#], Rulei Guo[1,2], Ni Tang[3,4], Zhan Peng[1,2], Hao Feng[1,2], Xiaobo Li[1,2], Jianfeng Zang[3,4,*], Nuo Yang[1,2,*]
[1]State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China
[2]Nano Interface Center of Energy (NICE), School of Energy and Power Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, People's Republic of China
[3]School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China
[4]Innovation Institute, Huazhong University of Science and Technology (HUST), Wuhan 430074, People's Republic of China

#Xiandong Chen and Meng An contributed equally to this work.
*Corresponding authors: N.Y. (nuo@hust.edu.cn) J. F. Z. (jfzang@hust.edu.cn)

ABSTRACT

The thermal properties of organic membranes attract much attention due to the fact that heat dissipation in electronic devices limits their functionality and reliability. Here, we enhance the thermal conductivity of polyvinyl alcohol (PVA) membrane using nano-fibers fabricated by electrospinning. Measured by the 3-Omega method, the results show that the effective thermal conductivity of the electrospinning membranes (with/without Cu nanoparticles) are as high as 0.7 W/m-K at room temperature which is as twice as the value of thermal conductivity of amorphous spin-coated PVA membrane (0.35 W/m-K). The mechanism of enhancement are that, compared with amorphous membrane, the phonon scattering is attenuated and the crystallinity is improved in the electrospinning process. Our studies bring new insights in designing new kind of membrane with high thermal conductivity.

INTRODUCTION

Polymers are widely used in our daily life as well as in industry such as printed circuit boards (PCBs) [1], thermal interface materials (TIMs) [2], and device bases/holders [3] owing to the advantages such as cheap cost, insulation and easy processing. However, its low thermal conductivity largely affects the capability and stability of electronic devices [4, 5]. PVA is one of the most commonly used macromolecule material in industry, amorphous PVA is regarded as heat insulator for its low thermal conductivity(~0.3 W/m-K) [6]. However, Sheng Shen [7] measured the thermal conductivity of single chain PE using SThM in 2010, the thermal conductivity is as high as 104 W/m-K, which is three magnitude higher than that of bulk PE. Others also made organic aligned nano-fiber [8] and membrane [9] with relatively high thermal conductivity. It shows that polymers have the potential to be used for heat dissipation in electric devices. Some results show that adding carbon nanotubes [10] and metallic oxide nanoparticles [11] is positive to the enhancement of thermal conductivity, do the nano-particles have positive effect on the thermal conductivity of nano-fiber membrane? In our study, we fabricated PVA spin coated membrane, electrospinning PVA nano-fiber membrane and electrospinning PVA nano-fiber membrane mingled with Cu nano-particles, then we measured the thermal conductivity of these membranes using the 3-

Omega method. The effective thermal conductivity of electrospinning membranes are greatly enhanced due to the attenuation of phonon scattering.

EXPERIMENTAL DETAILS

PVA powders were dissolved in DI water. The concentration was 8wt%. We fabricated the spin-coating PVA membrane which was served as the comparison at first. The silica deposited with heater served as substrate, the rotating speed was 3500 r/min and the rotating time was 30s, we repeated spin-coat process for four times to get the membrane. The nano-fiber membrane was fabricated using electrospinning [12, 13], the thickness was 8.1μm measured using step profiler. We mixed Cu particles and PVA powders to form 8wt% solution using magnetic stirring, the mass ratio of Cu particles to PVA was 1:8. The nano-fiber membrane with Cu particles was prepared using the same parameters in the electrospinning process, the thickness was 10μm.

The thermal conductivity was measured using the 3-Omega method [14-22]. The principle of the method can be seen in ref.12-20, the schematic diagram of the experimental configuration is shown in Fig. 1(a). In the differential model [15] or analytical model [17], the heater has to be deposited on the measured membrane directly. However, the heater is difficult to be deposited on the membrane with rough surface because the heater may not be continuous. In our study, we measured the thermal conductivity of PVA nano-fiber membrane using the two-direction asymmetric heat transfer model [18-22].
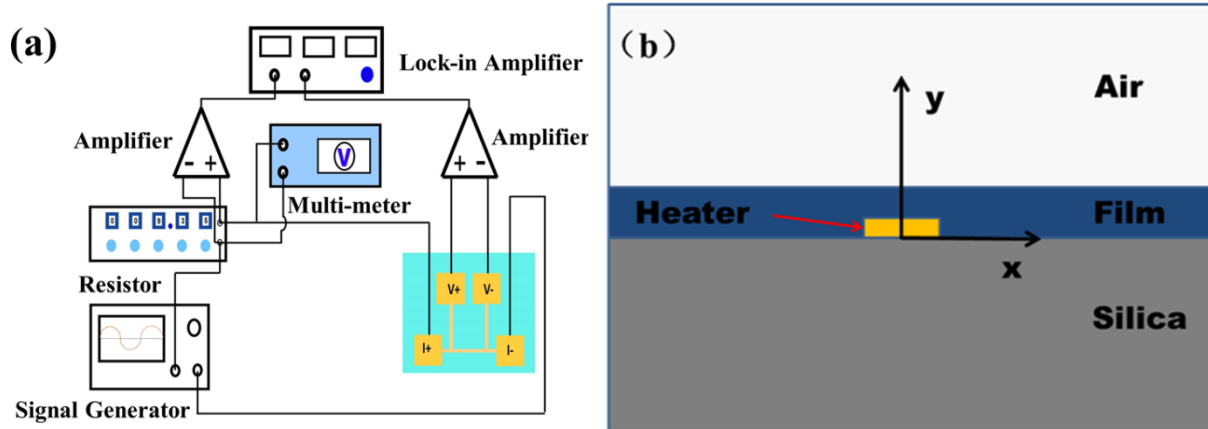
Figure 1. (a) The schematic diagram of the experimental configuration. An AC current from the signal generator (33509B) passes though the heater and the adjustable resistor (ZX74). The voltage signals of the wire and the resistor are then input into the lock-in amplifier (SR830) through the differential amplifiers (AMP03). The resistor is adjusted to balance the 1ω voltage signal of the heater because the 1ω voltage is thousands of times larger than the 3ω voltage. The Lock-in amplifier gets the 3ω voltage signal through the differential input A-B, the multi-meter (34401A) is used to measure the 1ω voltage; (b) The sketch graph of the experimental model, the materials along y-direction are fused quartz, metal line, the membrane (film) and air, respectively.

The experimental model is shown in Fig. 1(b), convection and radiation are neglected as the temperature rise is small in the experiment (only about 1-2 K) [14]. The metal heater was deposited on the 2 mm thick silica using electron beam evaporation with a 10 nm thick chromium adhesion layer and a 90 nm thick gold layer. The width and the length of the heater were 21.6 μm and 2013 μm, respectively. The membrane was placed upon the heater. The membrane was much bigger than

the heater. The heater was between the silica substrate and the membrane. Then the whole sample was wetted using acetone (PVA is insoluble in acetone). After that, the substrate was put on the heating stage heated at 70 °C for about 2 hours in order to dry the membrane and then cooled down to room temperature. We measured the thermal conductivity of the three membranes one by one using the same approach. We compared the measured results to find the most effective way to get polymer membrane with high thermal conductivity.

The relationship of the temperature rise of the heater, 3ω voltage and 1ω voltage is [14],

$$\Delta T(2\omega) = \frac{2V_{3\omega}}{V_{1\omega}\beta} \tag{1}$$

$V_{1\omega}$ is the 1ω voltage, $V_{3\omega}$ is the in-phase 3ω voltage, β is the temperature coefficient of the metal wire. The temperature rise of the metal heater is [23]

$$\Delta T(2\omega) = \frac{P}{\pi l} \int_0^\infty \frac{1}{2\gamma_1} \frac{B^+ + B^-}{A^+B^- - A^-B^+} \frac{\sin^2(\lambda b)d\lambda}{(\lambda b)^2} \tag{2}$$

Where P is the power of the metal heater, l and b are length and half-width of the heater, respectively. λ is the integral variable in Fourier space, $\gamma_i = \kappa_i \sqrt{\lambda^2 + i2\omega/\alpha_i}$, $\alpha_i = \kappa_i / C_i$, C_i is the volume heat capacity of the ith layer, subscript 0, 1, 2 ,3 are the silica, the heater, the fabricated membrane, air, respectively. A^+, A^-, B^+ and B^- are dimensionless parameters solved using a recursive matrix method, A^+ and A^- are(A^+ is the top item in the matrix, A^- is the beneath item)

$$\tilde{A} = \frac{1}{2\gamma_1} \begin{pmatrix} \gamma_1 + \gamma_0 & \gamma_1 - \gamma_0 \\ \gamma_1 - \gamma_0 & \gamma_1 + \gamma_0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{3}$$

B^+ and B^- are (B^+ is the top item in the matrix, B^- is the beneath item)

$$\tilde{B} = \frac{1}{2\gamma_1} \begin{pmatrix} \gamma_1 + \gamma_2 - \gamma_1\gamma_2 R & \gamma_1 - \gamma_2 + \gamma_1\gamma_2 R \\ \gamma_1 - \gamma_2 - \gamma_1\gamma_2 R & \gamma_1 + \gamma_2 + \gamma_1\gamma_2 R \end{pmatrix} \begin{pmatrix} e^{-\mu_2 d_2} & 0 \\ 0 & e^{\mu_2 d_2} \end{pmatrix} \frac{1}{2\gamma_2} \begin{pmatrix} \gamma_2 + \gamma_3 & \gamma_2 - \gamma_3 \\ \gamma_2 - \gamma_3 & \gamma_2 + \gamma_3 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{4}$$

$\mu_i = \sqrt{\lambda^2 + i2\omega/\alpha_i}$, it is the penetration depth in Fourier space [14], R is the interfacial thermal resistance between the metal line and the membrane. As the interfacial thermal resistance between the metal heater and the substrate is about 10^{-7} to 10^{-8} m²-K/W [24], it is negligible [25]. The unknown parameters in equation (2) are the thermal conductivity, the heat capacity of the membrane and the contact resistance between the membrane and the heater. These unknown parameters can be extracted using a multi-parameter fit of the experimental data.
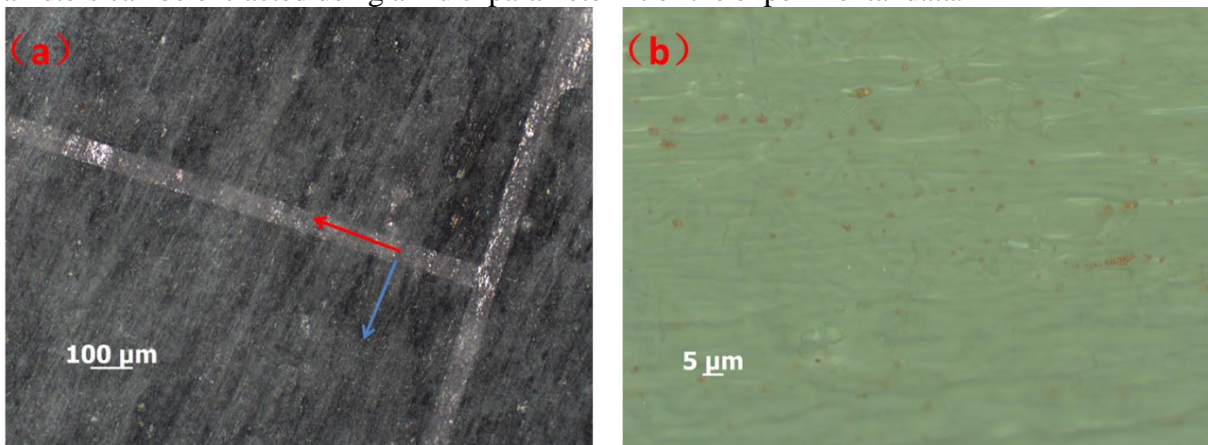
Figure 2. (a) The topography of the PVA nano-fiber membrane under microscope; (b) The topography of the PVA mingled with Cu nano-particles nano-fiber membrane under microscope.

Firstly, we measured the temperature coefficient of the metal line, β=0.002±0.0001 K^{-1}, which was shown in Fig. 3(a). Secondly, 3-Omega method was used to measure the thermal conductivity and volume heat capacity of the fused silica substrate. The thermal conductivity of the substrate and the volume heat capacity were 1.39±0.07 W/m-K and 1.60 ±0.11 MJ/m^3-K, respectively, which were analyzed using the two-direction heat transfer model. The results were shown in Fig. 3(b), which were consistent with Cahill's results [14].
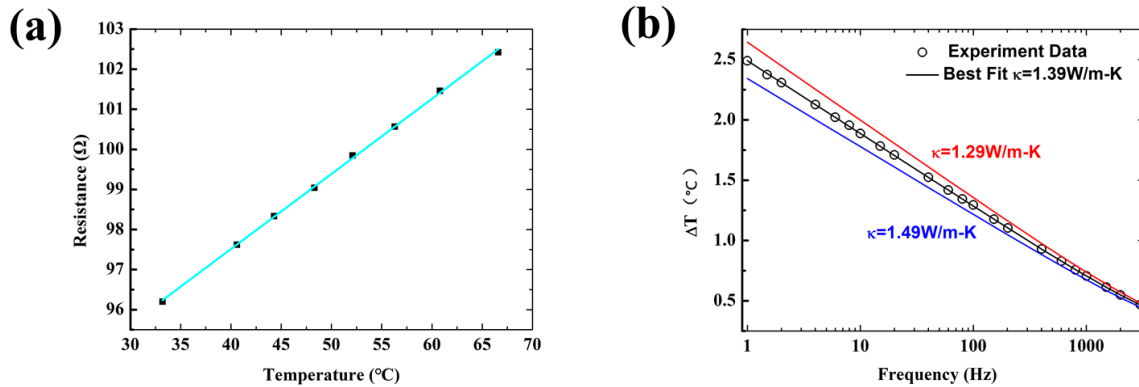
Figure 3. (a) The temperature coefficient of the metal line; (b) Data fitting of the thermal conductivity of silica substrate at room temperature

The sensitivity of the signal to different thermo-physical properties was quantified by considering the differential change in the measured temperature rise caused by the differential perturbation in a specific thermo-physical property x of a nominal value. The sensitivity was defined as [21]:

$$S_x = \frac{\partial \ln(\Delta T)}{\partial \ln(x)} \tag{5}$$

It was noted that the most sensitive range was 10-1000 Hz which was plotted in Fig. 4. Previous studies had demonstrated that this range could ensure that the penetrate depth was much bigger than the thickness of membrane and the half-width of the heater while it was much smaller than the thickness of the substrate [15]. Firstly, we measured thermal conductivity and volume heat capacity of spin coated PVA membrane ,the results were 0.33 W/m-K and 1.68 MJ/m^3-K, respectively, which were consistent with Xie's results [26], the interfacial thermal resistance was 8.8×10^{-6} m^2-K/W. The thermal properties of PVA nano-fiber membrane were measured using the same method. The thermal conductivity and volume heat capacity of the membrane were 0.24 W/m-K and 0.62 MJ/m^3-K, respectively. However, the interfacial thermal resistance was 1.3×10^{-4} m^2-K/W, which was a magnitude higher than that of the spin coated PVA membrane. The reason might be that the contact area of PVA nano-fiber membrane was much smaller than that of spin coated PVA membrane. The thermal conductivity of PVA nano-fiber membrane mingled with Cu nano-particles was shown in Fig. 4(b).

The effective thermal conductivity [27] of the membrane was defined as:

$$\kappa_{measured} = x\kappa_{effective} + (1-x)\kappa_{air} \tag{6}$$

$$(C_P\rho)_{measured} = x(C_P\rho)_{effective} + (1-x)(C_P\rho)_{air} \tag{7}$$
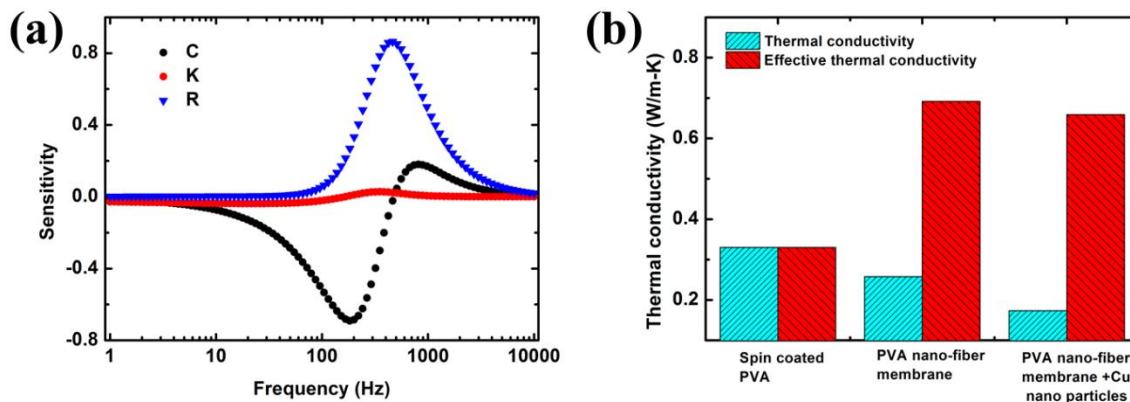
Figure 4. (a) The sensitivity of thermal conductivity, volume heat capacity and contact resistance of membrane; (b) Thermal conductivity of PVA nano-fiber membrane and PVA nano-fiber membrane mingled with Cu nano-particles

The subscript "measured" mean the results that were measured using the 3-Omega method. The heat capacity of air was small compared to the PVA and the effective thermal conductivity of the membrane can be calculated using Eq. (7), the results were shown in Fig. 4(b).

It is found that the effective thermal conductivity of the nano-fiber membrane is 0.7 W/m-K, which is two times larger than that of the spin coated PVA membrane. The reason can be that the polymer chains are stretched 1000 times longer than that of the original curled molecules using electrospinning, which enhances the chain alignment and crystallinity. The increased thermal conductivity originates from the attenuated phonon scattering compared with amorphous structure. The effective thermal conductivity of nano-fiber membrane mingled with nano-particles is 0.68 W/m-K, it doesn't show enhancement because there is no "effective heat transfer channel" when we just mingled the particles with PVA solution. The weak van der Waals force between the fibers and the particles contributes little to the heat transfer in the membrane. Maybe the thermal conductivity of the membrane can be enhanced if the surface of nano-particles is chemical modified [28], PVA can reacts with nano-particles in that situation, the force between the fibers and the particles is greatly enhanced which increases thermal conductivity.

CONCLUSIONS

In the summary, we measured the thermal conductivity of PVA nano-fiber membrane and PVA nano-fiber membrane mingled with Cu nano-particles using the 3-Omega method. It was found that the thermal conductivity of the PVA nano-fiber membrane was two times higher than that of PVA spin coated membrane. The reason is that the stretched polymer chains attenuate phonon scattering and thus increase the mean free path of phonons. Besides, it was found that adding Cu nano-particles was not an effective approach to increase thermal conductivity because there were no "effective heat transfer channels" between the chains. Our results provide a good strategy for designing the organic membrane with high thermal conductivity.

ACKNOWLEDGMENTS

REFERENCES

[1]   J. Liu, C. Yang, H. Wu, Z. Lin, Z. Zhang, et al., *Energy & Environmental Science* **7** 3674 (2014).

[2]   T. Luo and J. R. Lloyd, *Advanced Functional Materials* **19** 587 (2009).

[3]   K. Soygun, G. Bolayir, and A. Boztug, *Journal of Advanced Prosthodontics* **114** 153 (2013).

[4]   L. Derue, *Eastern Anthropologist* **32** 55 (1979).

[5]   A. L. Moore and L. Shi, *Materials Today* **17** 163 (2014).

[6]   G. I. Makhatadze, Physical properties of polymers, *Springer* 2007.

[7]   S. Shen, A. Henry, J. Tong, R. Zheng, and G. Chen, *Nature nanotechnology* **5** 251 (2010).

[8]   B. Y. Cao, Y. W. Li, K. Jie, H. Chen, X. Yan, K. L. Yung, and C. An, Polymer **52** 1711 (2011).

[9]   H. Ghasemi, N. Thoppey, X. Huang, and J. Loomis, *IEEE Itherm Conference* 235 (2014).

[10]   A. A. Balandin, *Nature materials* **10** 569 (2011).

[11]   G.-H. Kim, D. Lee, A. Shanker, L. Shao, M. S. Kwon, D. Gidley, J. Kim, and K. P. Pipe, *Nature materials* **14** 295 (2015).

[12]   D. Li and Y. Xia, *Advanced Materials* **16** 1151 (2004).

[13]   J. Ma, Q. Zhang, A. Mayo, Z. Ni, H. Yi, Y. Chen, R. Mu, L. M. Bellan, and D. Li, *Nanoscale* **7** 16899 (2015).

[14]   D. G. Cahill, *Review of Scientific Instruments* **61** 802 (1990).

[15]   D. G. Cahill, M. Katiyar, and J. Abelson, *Physical Review B* **50** 6077 (1994).

[16]   D. W. Oh, A. Jain, J. K. Eaton, K. E. Goodson, and J. S. Lee, *International Journal of Heat & Fluid Flow* **29** 1456 (2008).

[17]   T. Borca-Tasciuc, A. Kumar, and G. Chen, *Review of Scientific Instruments* **72** 2139 (2001).

[18]   A. Feldman, *High Temperatures-High Pressures* **31** 293 (1999).

[19]   J. H. Kim, A. Feldman, and D. Novotny, *Journal of Applied Physics* **86** 3959 (1999).

[20]   P. E. Hopkins, B. Kaehr, L. M. Phinney, T. P. Koehler, A. M. Grillet, D. Dunphy, F. Garcia, and C. J. Brinker, *Journal of Heat Transfer* **133** 989 (2011).

[21]   M. T. Barako, S. Roypanzer, T. S. English, T. Kodama, M. Asheghi, T. W. Kenny, and K. E. Goodson, *ACS Applied Materials & Interfaces* **7** 216 (2015).

[22]   M. T. Barako, A. Sood, C. Zhang, J. Wang, T. Kodama, M. Asheghi, X. Zheng, P. V. Braun, and K. E. Goodson, *Nano Letters* **16(4)** 2754 (2016).

[23]   M. L. Bauer and P. M. Norris, *Review of Scientific Instruments* **85** 064903 (2014).

[24]   D. G. Cahill, W. K. Ford, K. E. Goodson, G. D. Mahan, A. Majumdar, H. J. Maris, R. Merlin, and S. R. Phillpot, *Journal of Applied Physics* **93** 793 (2003).

[25]   T. Tong and A. Majumdar, *Review of Scientific Instruments* **77** 104902 (2006).

[26]   X. Xie, D. Li, T. H. Tsai, J. Liu, P. V. Braun, and D. G. Cahill, *Macromolecules* **49(3)** 972 (2016).

[27]   J. P. Feser, J. S. Sadhu, B. P. Azeredo, K. H. Hsu, J. Ma, et al., *Journal of Applied Physics* **112** 085204 (2012).

[28]   C. Chen, H. Wang, Y. Xue, Z. Xue, H. Liu, X. Xie, and Y.-W. Mai, *Composites Science and Technology* **128** 207 (2016).