Supporting Information:

PDMS Nanocomposites for Heat Transfer Enhancement in

Microfluidic Platforms

Pyshar Yi,*a Robiatun A. Awang, Wayne S. T. Rowe, Kourosh Kalantar-zadeh,*a and

Khashayar Khoshmanesh*a

^{*a*} RMIT University, School of Electrical and Computer Engineering, Melbourne, Victoria 3001, Australia.

E-mail: pyshar.yi@gmail.com

kourosh.kalantar@rmit.edu.au,

khashayar.khoshmanesh@rmit.edu.au

Supplementary Information 1: Improving the dispersion of Al₂O₃ nanoparticles in PDMS

In order to improve the dispersion of Al_2O_3 (average diameter of <50 nm) in PDMS, the mixing procedure of nanocomposites has been improved. Instead of manual stirring, a shaker (Vortex mixer - Select BioProducts, Australia) is applied to mix the Al_2O_3 nanoparticles with PDMS matrix at various speeds of 1200-2200 rpm for 15 min. Next, the sample is placed in an ultrasonic bath (ultrasonic power = 180 W) for 30 min to minimize the aggregation of Al_2O_3 within the matrix. Afterwards, the PDMS curing/crosslinking agent (Sylgard 184, Dow Corning) is added to the mixture in a 10:1 ratio. The sample is then shaken by the shaker at a speed of 1200 rpm for 10 min. The sample is degassed for 30 min at a pressure of 25 kPa in order to remove the trapped air bubbles using a vacuum oven. The PDMS/ Al_2O_3 nanocomposite is poured onto the master and cured on a hot plate with a temperature of 70 °C for 20 min.

Fig. S1 shows the homogeneity and roughness of PDMS/Al₂O₃ nanocomposites at 10% *w/w*, obtained by the abovementioned process. As can be seen from Fig. S1(a), by increasing the speed of the shaker, the Al₂O₃ nanoparticles are distributed more uniformly within the PDMS matrix, and the agglomeration of Al₂O₃ nanoparticles has decreased. For example, by increasing the speed of the shaker from 1200 to 2200 rpm, the average dimension of Al₂O₃ agglomerates reduces from ~70 to ~20 nm (Fig. S1(a(i) and (iii))).

The roughness of the nanocomposites is also investigated by AFM probing (Fig. S1(b)). Results demonstrate the decrease in the roughness by increasing the speed of shaker to 2200 rpm. For instance, by increasing the speed of the shaker from 1200 to 2200 rpm, the roughness reduces from ± 200 to ± 50 nm (Fig. S1(b(i) and (iii))).



Fig. S1 (a) SEM images of 10% *w/w* **PDMS/Al₂O₃ nanocomposites at various speeds of the shaker**: (i) 1200, (ii) 1700 and (iii) 2200 rpm. (b) AFM images of a 10% *w/w* PDMS/Al₂O₃ nanocomposites at various speeds of the shaker: (i) 1200, (ii) 1700 and (iii) 2200 rpm and (c) the variation of the maximum roughness of 10% *w/w* PDMS/Al₂O₃ nanocomposites at various speeds of the shaker.

Supporting Information 2: Thermal conductivity measurements of PDMS/MWCNT and PDMS/Al₂O₃ nanocomposites

Dispersion of nanoparticles in PDMS

MWCNT and Al₂O₃ nanoparticles (Sigma Aldrich, Australia) are used to form nanocomposites of PDMS. The MWCNT or Al₂O₃ nanoparticles are added into the PDMS matrix at desired concentrations and manually stirred for 10 min, followed by the sonication in an ultrasonic bath (Unisonics, Australia) for a further 20 min to mix thoroughly in order to obtain uniformity of distribution within a polymer matrix. The PDMS curing/crosslink agent (Sylgard 184, Dow Corning) is added to the mixture to form a 10:1 ratio. The sample is stirred manually for 10 min, and then degassed for 30 min in order to remove the trapped air bubbles using a vacuum oven.

The prepared PDMS/MWCNT or PDMS/Al₂O₃ nanocomposites are cured overnight at room temperature in a blue plastic tube (PUN tubing, FESTO) to provide the cylindrical shape of the nanocomposite. The tube is cut to provide a length to diameter ratio of larger than 5 and is blocked from one side using a microscopic glass slide. To ensure that heat conduction occurs only along the length of the cylindrical nanocomposites, we further insulate the sample tightly in a block of foam. The sample is then ready for measuring its thermal conductivity.

Experimental setup

An experimental setup for the thermal conductivity measurements is shown in Fig. S2. It consists of a hot plate, a cured mixture of nanoparticles in PDMS in the blue plastic tube wrapped around by the block of foam. To reduce measurement errors, we conduct experiments with different tubing lengths of 35 and 65 mm at different hot plate temperatures of 45, 65 and 95 °C. Each experiment is repeated at least three times. The hot plate is pre-heated to reach the desired temperatures. The sample is then placed on a hot plate for 30 min. Then the temperature of the hot plate and the tip of the sample are measured using an infrared thermal imaging camera. Assuming a one-dimensional heat transfer along the length of the tube, the thermal conductivity of the PDMS/MWCNT or PDMS/Al₂O₃ nanocomposites is calculated as below¹:

$$k\frac{(T_{hot} - T_{cold})}{l} = h(T_{cold} - T_{amb})$$
⁽¹⁾

where k is the thermal conductivity of the PDMS/MWCNT or PDMS/Al₂O₃ nanocomposites, l is the length of the tube, T_{hot} is the temperature of the hot plate in contact to the tube, T_{cold} is the average temperature at the tip of the PDMS/MWCNT or PDMS/Al₂O₃ nanocomposites, T_{amb} is the ambient temperature and h is the free convection coefficient which is assumed to be 10 W m⁻¹ K⁻¹.



Fig. S2 Experimental setup for thermal conductivity measurements of mixed nanoparticles in PDMS

Supporting Information 3: Thermal conductivity of PDMS/Al₂O₃ nanocomposites using larger size Al₂O₃ nanoparticles

We also investigated the thermal conductivity of the nanocomposites using larger Al_2O_3 nanoparticles with an average diameter of < 400 nm (Sigma Aldrich, Australia). The preparation of PDMS/ Al_2O_3 nanocomposites is the same as the nanocomposites prepared with smaller size. Also, the experimental setup and the measurements are conducted the same as those described in Supporting Information 2.

Fig. S3 demonstrates the variation of the thermal conductivity of the nanocomposite at different sizes and concentrations of Al_2O_3 nanoparticles. As can be observed, increasing the average size of Al_2O_3 from 50 to 400 nm reduces the thermal conductivity of the nanocomposite by approximately 10%. Although, the same concentration of Al_2O_3 is mixed within the PDMS matrix, the larger sizes of Al_2O_3 nanoparticles are not well-distributed within the matrix and create randomly distributed large clusters, disconnecting the bond between the particles, thus reducing the overall heat transfer efficiency within the composites.



Fig. S3 Variation of nanocomposites thermal conductivity with different sizes and concentrations of Al₂O₃ nanoparticles.

Supporting Information 4: Thermal conductivity investigations of PDMS/MWCNT nanocomposites



Fig. S4 Thermal conductivity of PDMS/MWCNT nanocomposites at various concentrations (0 to 10% *w/w*) of MWCNT.

Supporting Information 5: Specific heat capacity measurements for PDMS/Al₂O₃ nanocomposites

In order to determine the specific heat capacity of various PDMS/Al₂O₃ nanocomposites, we fabricate three rectangular blocks of 0, 2 and 10% *w/w* Al₂O₃ with a dimension of 50 mm \times 20 mm \times 2 mm (length \times width \times height).

The measurement begins by preheating the oven to \sim 53 °C. Once, the oven reaches its stable temperature, a block of PDMS or PDMS/Al₂O₃ nanocomposite is heated in the oven for 25 min to achieve a uniform temperature across the block. The block is then quickly placed under the infrared camera to record the temperature drop for 100 s; after the temperature of the block reaches the temperature of the ambient.

The heat capacity of the blocks is calculated using the lumped capacity method ², as summarized below. Assuming uniform temperature throughout the structure, the heat exchange between the block and the surrounding air can be expressed as below:

$$mc_p \frac{\partial T}{\partial t} = -h A(T_s - T_{\infty})$$
⁽²⁾

where *T* is temperature, *m* is the mass of the block, c_p is the specific heat capacity of the block, *t* is time, *h* is a free convection coefficient (taken a constant value as 10 W m⁻¹ K⁻¹), *A* is the total surface area of the block, and T_{∞} is the ambient temperature.

Assuming that the initial temperature is T_o , the transient temperature of the block can be expressed as below:

$$\Rightarrow (T - T_{\infty}) = (T_o - T_{\infty}) \exp(\frac{-hA}{mc_p}t)$$
(3)

which can be written as below:

$$\Rightarrow \ln (T - T_{\infty}) = \ln (T_o - T_{\infty}) - \frac{hA}{mc_p}t$$
(4)

and in the logarithmic scale, the slope of the line can be calculated as: $-\frac{hA}{mc_p}$

The mass of the blocks is weighted using a digital scale (KERN EW 420-3NM, Germany). The results of our measurement are summarized in Table S1 and shown in Fig. S5.

Material	Mass, m	Area, A	Δt	Slope	c _p
	(g)	(m ²)	(s)		(KJ kg ⁻¹ K ⁻¹)
PDMS	2.16	12.8×10^{-4}	100	-0.0043	1.38
PDMS +	2 79	12.8×10^{-4}	100	_0.00350	1 31
2% Al ₂ O ₃	2.19	12.0 × 10	100	0.00550	1.51
PDMS +	3 1 1	12.8×10^{-4}	100	-0.0032	1 29
10% Al ₂ O ₃	5.11	12.0 * 10	100	0.0052	1.27



Fig. S5 Temperature drops of PDMS and PDMS/Al₂O₃ nanocomposites in log scale over time. The results are based on the averaged temperatures obtained by three separate experiments for each case.

Supporting Information 6: Elasticity measurements for PDMS/Al₂O₃ nanocomposites

We determine the elasticity (*E*) of PDMS and PDMS/Al₂O₃ nanocomposites by using a Universal Testing Machine (UTM; WL 2100; Instron, Norwood, MA) according to KS M 6518 test method ³(see Fig. S6(a)). The geometry and dimensions of the specimen stripe are shown in Fig. S6(b). Each specimen is locked to a force gauge and can be programmed to move along the vertical axis with a load speed of 50 mm min⁻¹ while the force gauge is connected to a computer for real time monitoring of the force. The specimen is slowly stretched until it breaks. At that instant, the specimen elasticity, *E*, is automatically calculated from the slope of the force against stretch of the specimen. After testing 5 specimens, the computer gives the average result of the elasticity for each individual sample.



Fig. S6 (a) Universal testing machine and (b) 3D geometry of PDMS or PDMS/Al₂O₃ nanocomposite specimen

Supporting Information 7: CFD simulation results at 40 µl min⁻¹

In order to calculate the variations of temperature within the microfluidic platform, we solve the energy equations within the microchannel, PDMS or PDMS/Al₂O₃ nanocomposites, glass substrate, and heater. However, as the microchannel is filled with liquid, the energy equation is linked to the velocity of liquid flowing through it, and therefore the continuity and momentum equations should also be solved, as given below⁴:

$$\nabla \cdot \vec{U} = 0 \tag{6}$$

Liquid inside the microchannel:
$$\rho_{liquid}(\vec{U}\cdot\nabla)\vec{U} = -\nabla P + \mu_{liquid}\nabla^2\vec{U}$$
 (7)

$$(\rho c_p)_{liquid} (\vec{U} \cdot \nabla) T = k_{liquid} \nabla^2 T$$
(8)

PDMS or PDMS/Al₂O₃ nanocomposites:
$$k_{PDMS} \nabla^2 T = 0$$
 (9)

Glass substrate:
$$k_{glass} \nabla^2 T = 0$$
 (10)

Heater:
$$k_{heater} \nabla^2 T + \mathcal{O} = 0$$
 (11)

in which \vec{U} , *P* are the velocity and pressure of the liquid, *T* is the temperature, ρ , μ , c_p and *k* are the density, dynamic viscosity, heat capacity and thermal conductivity, respectively, and \mathcal{B} is the heat per volume generate by the heater.

The boundary conditions applied for the microchannel include ambient pressure at the inlet, a flow rate of 40 μ l min⁻¹ at the outlet, and no-slip at the walls. The temperature of the inlet liquid is set to ambient temperature while a fully developed condition is assumed at the outlet to

calculate the temperature $(\frac{\partial T}{\partial x} = 0)$. The temperatures are coupled at the interface of microchannel-PDMS, microchannel-glass, PDMS-glass and heater-PDMS. It is assumed that free convection occurs at the external surfaces of the microfluidic platform exposed to the environment:

External surfaces of the system:
$$k_{surface} \frac{\partial T}{\partial n} = h(T - T_{\infty})$$
 (12)

in which *n* is the vector normal to the surface, *h* is the free convection coefficient which is set to 10 W m⁻¹ K⁻¹ and T_{∞} is the ambient temperature which is set to 298 K.

Simulations are conducted in three different cases to be in line with the experiments: (i) pure PDMS, (ii) PDMS/Al₂O₃ nanocomposte with 2% w/w of Al₂O₃ nanoparticles, and (iii) PDMS/Al₂O₃ nanocomposte with 10% w/w Al₂O₃ nanoparticles.

Supporting Information 8: Thermal performances of PDMS/Al₂O₃ nanocomposites at various concentrations and flow rates

The variation of temperature along arbitrary lines *B* (hot side wall of the microchannel) and *C* (cold side wall of the microchannel) at different flow rates (10, 40 and 120 μ l min⁻¹) are presented in Fig. S7(a) and (b), respectively. Similar to the observation of line *A*, when comparing the microfluidic system with 10% *w/w* Al₂O₃ nanoparticle operating at a low flow rate of 10 μ l min⁻¹ to the system with pure PDMS at a high flow rate of 120 μ l min⁻¹, the temperature drop of 3 and 4 K along line *B* and *C*, respectively, are measured.



Fig. S7 Variation of temperature for various concentrations of PDMS/Al₂O₃ nanocomposites at different flow rates along line *B* and *C*. (a) line *B* and (b) line *C* (shown in Fig. 6 (a))

References

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