

Molecular Design for Highly Matched and Bonded Interface Achieves Enhanced Thermal Boundary Conductance

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1. Experimental Section

1.1. Materials

Adipic dihydrazide (AD, 99%), isophorone diisocyanate (IPDI, mixture of isomers, 99%), allyl glycol (usafdo-47, 98%), ditin butyl dilaurate (T12, 95%), N, N-dimethylbenzylamine (99%) diiodomethane (98%), ethylene glycol (GC, 99.9%) and polymethyl methacrylate ether solution (6%) were purchased from Aladdin (China). N, N-dimethylacetamide (DMAc, 99.8%) was purchased from energy chemical (China). Thioctic acid (TA, 99%) and methylhexahydrophthalic anhydride were purchased from Shanghai Maclin Biochemical Technology Co., LTD. CYD-128 was purchased from China Petroleum & Chemical Corporation. SylgardTM 184 silicone elastomer kit was purchased from dow chemical company. All the starting reagents and solvents used in the syntheses were used without further purification.

1.2. Synthesis

1) Synthesis of the PU-TA elastomers

The typical synthetic routes for the PU-TA polymers are shown in Figure S1 and described in detail as follows. A three-neck round bottom flask equipped with a mechanical stirrer was charged with 0.025 mol AD, 30 ml DMAc, 0.0774g T12, and 0.05 mol IPDI, followed by heating at 70 °C and stirring for 2 h to obtain adipic dihydrazide-isophorone diisocyanate (AD-NCO). Next, 0.05 mol usafdo-47 and 20 ml DMAc were simultaneously added into the AD-NCO, followed by heating at 70 °C and stirring for 2 h to obtain adipic dihydrazide-isophorone diisocyanate-allyl glycol (AD-NCO-AG). Another single-neck round bottom flask equipped with a mechanical stirrer was charged with TA (0.0242 mol), followed by heating at 160 °C for 10 min. When the TA was melted, AD-NCO-AG (0.0484 mmol for PU-TA@500-1; 0.0605 mmol for PU-TA@400-1; 0.08067 mmol for PU-TA@300-1; 0.121 mmol for PU-TA@200-1; 0.242 mmol for PU-TA@100-1; 1.613 mmol for PU-TA@15-1), a certain amount of T12 remained in the AD-NCO-AG and DMAc (10 ml) were added into the flask. The reaction system was further kept at 160 °C for 20 min. The as-obtained polymer solutions were poured into Teflon template and then heated in oven at 80 °C for 12 h, finally a series of different crosslinking PU-TA was obtained. When the theoretical mole ratio of TA and prepolymer was 500:1, PU-TA was marked as PU-TA@500-1. Naming method of PU-TA@400-1, PU-TA@300-1, PU-TA@200-1, PU-TA@100-1 and PU-TA@15-1 was the same as the method as above.

2) Synthesis of the PU-TA thermal interface

Physical vapor deposition (PVD) technology was employed to deposit aluminum (Al) layer on the surface of quartz glass surface with a thickness of 200 microns. Al was grown as thin layers (46 ± 1 nm) on the surface of quartz glass by magnetron sputtering (PRO line PVD 75; Kurt J. Lesker Company, Jefferson Hills, PA, USA) at room temperature (Figure S4). In each experiment, a vacuum of about 1×10^{-6} mTorr must be reached before argon was injected into the chamber. The obtained thickness of Al grew out at PVD 75 for 150 s at the power of 500 W. Polymethyl methacrylate (PMMA) ether solution will be used to form a protective layer on the surface of the Al layer to prevent metal oxidation. PMMA can be removed by acetone before next use. PU-TA polymer solutions was deposited on the Al layer via spin-coating method at 400 rpm on Model WS-650MZ-23NPPB. The obtained samples were heated in oven at 80 °C for 12 h, finally a series of different crosslinking PU-TA thermal interface were synthesized.

3) Synthesis of the PDMS and EP and its thermal interface with Al

SylgardTM 184 silicone elastomer kit was spin-coated on Al layer. EP was synthesis by mixing 10 g CYD-128, 1g methylhexahydrophthalic anhydride and 0.055 g N, N-dimethylacetamide, and then spin-coated on Al layer. Both samples were heated in oven at 125 °C for 1 h and 145 °C for 3 h.

2. Supplementary Figures and Tables

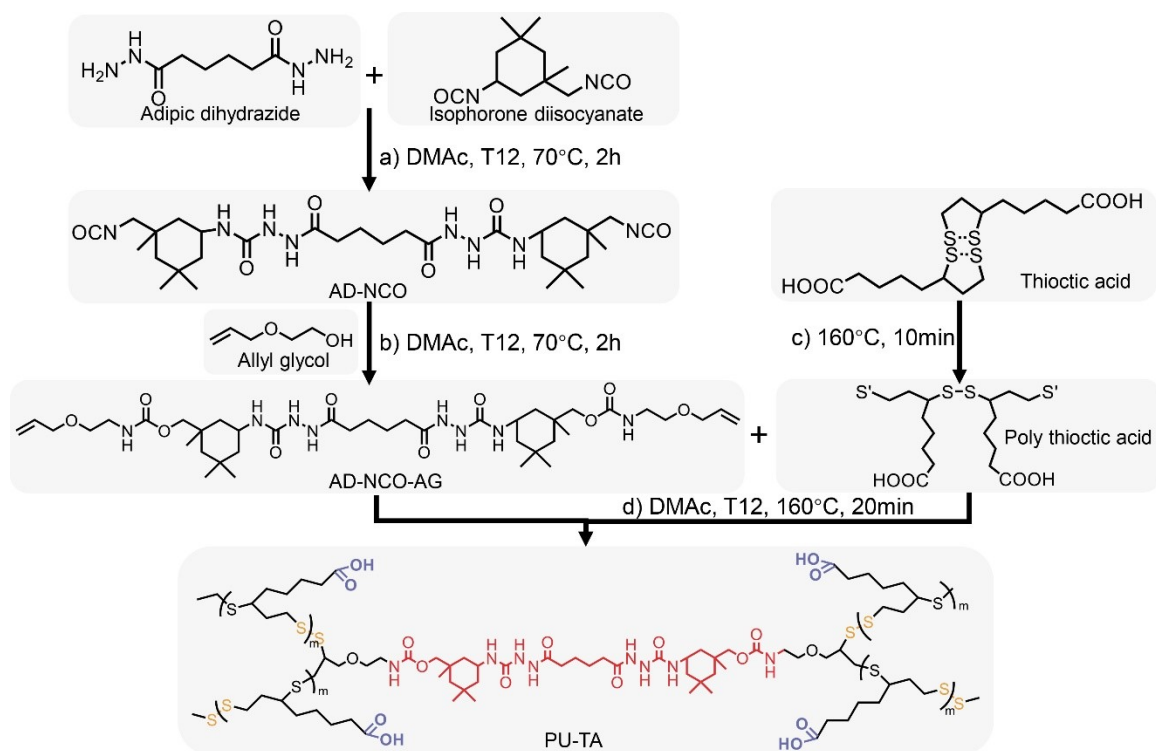


Figure S1. Synthetic routes of the PU-TA polymers.

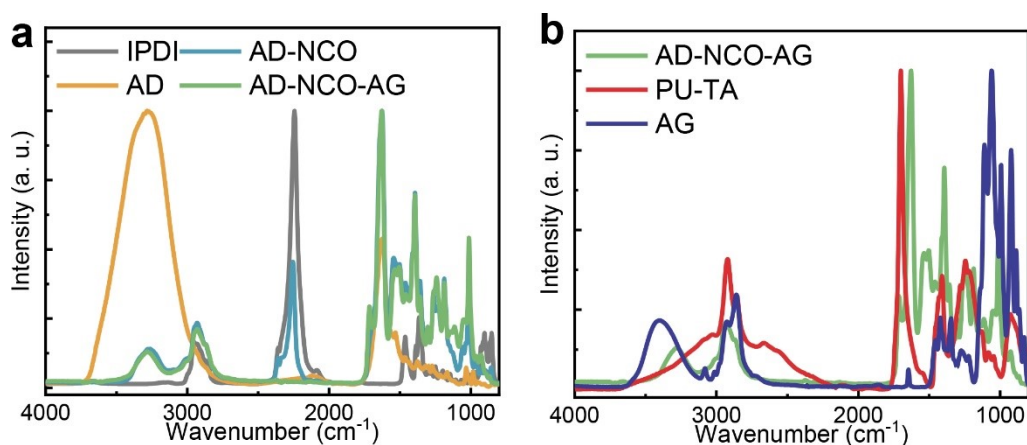


Figure S2. Fourier transform infrared spectrometer (FTIR) spectra of (a) 4000-1000 cm⁻¹ of IPDI, AD, AD-NCO, and AD-NCO-AG, and (b) 4000-1000 cm⁻¹ of AD-NCO-AG, PU-TA, and AG.

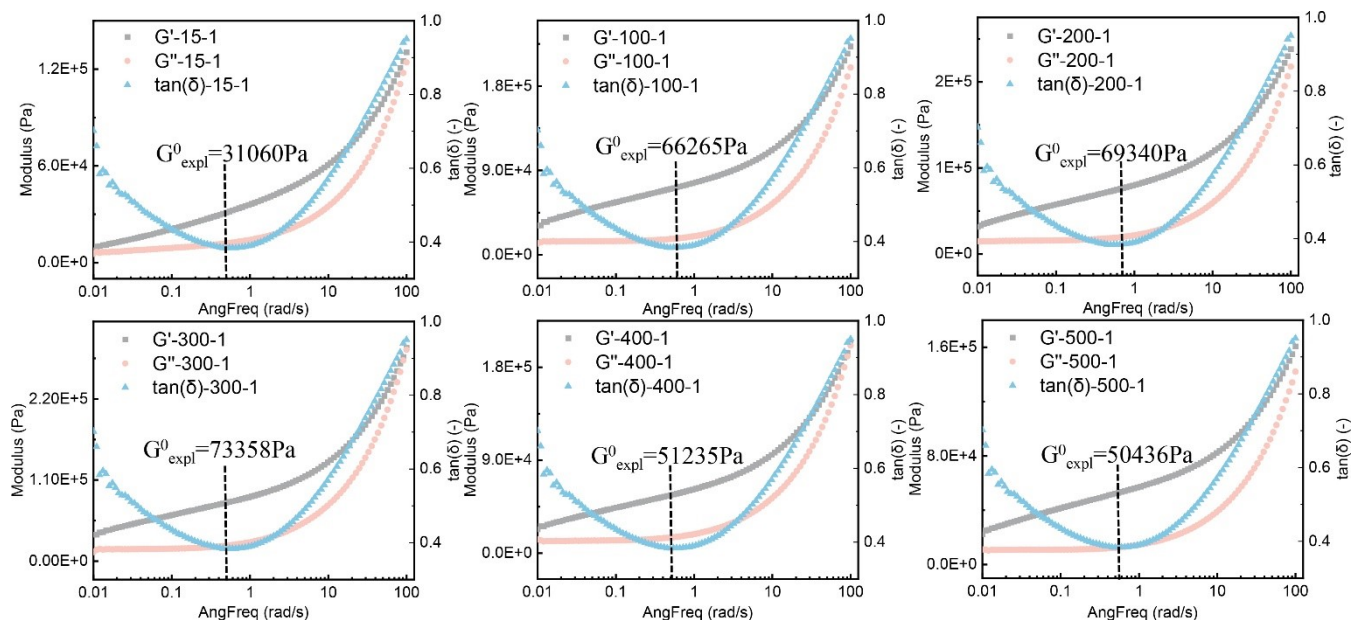


Figure S3. The storage modulus (G'), the loss modulus (G'') and loss factor ($\tan(\delta)$) of PU-TA with different V_e . PU-TA@15-1 in figure was abbreviated as 15-1, and others were similar to the above.

The storage modulus (G') in Fig. S3 were larger than the loss modulus (G'') indicating that the bulk polymer preferred exhibiting the properties of elastic solids.

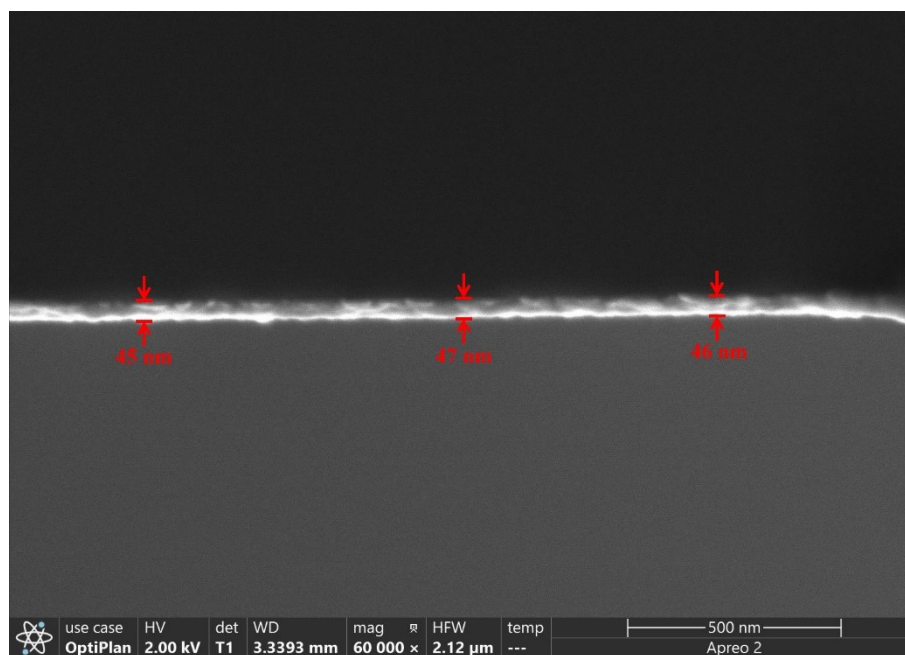


Figure S4. SEM image of the cross section of a substrate (Al/ quartz glass).

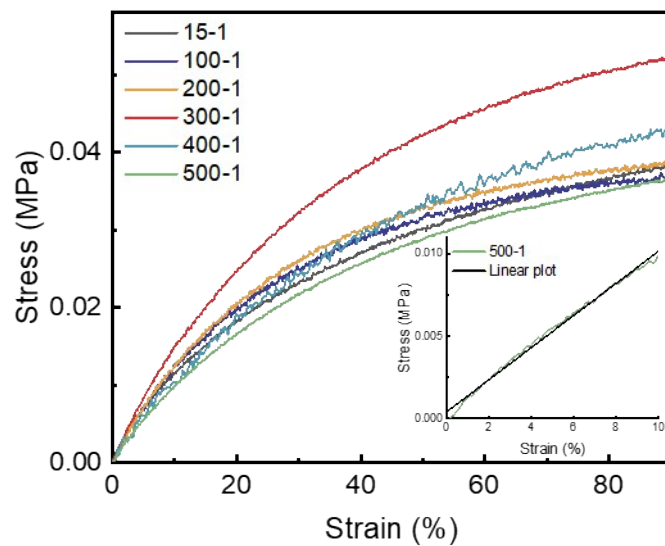
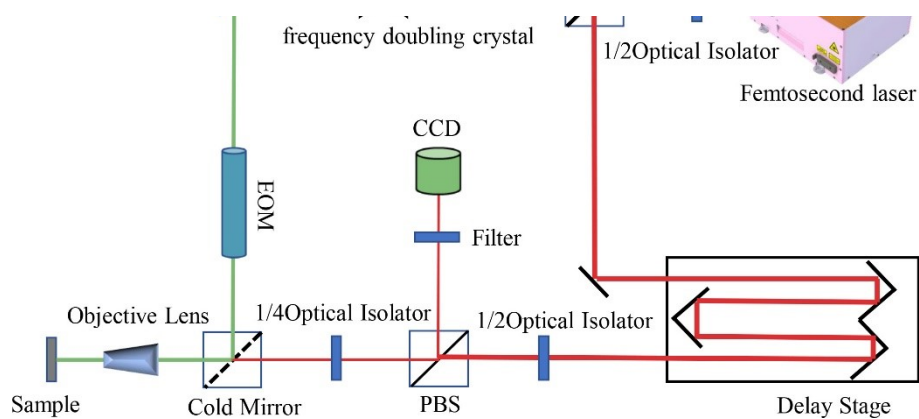


Figure S5. Stress-strain curves about PU-TA with different molar ratio of prepolymer 3 and prepolymer 2.

Figure S6. The schematic diagram of a typical TDTR setup.



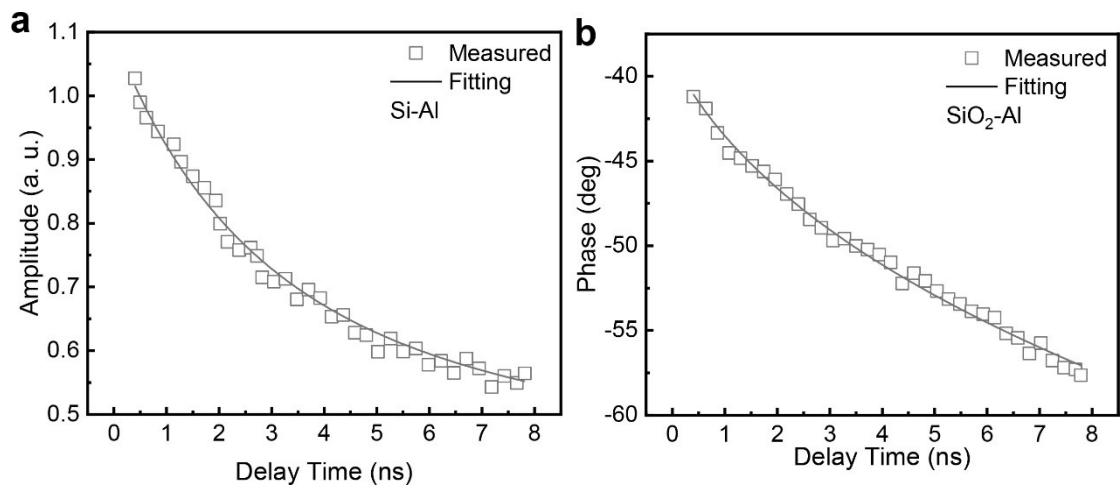


Figure. S7. (a) Measured and fitting curves of Si/Al; (b) Measured and fitting curves of fused silica/Al

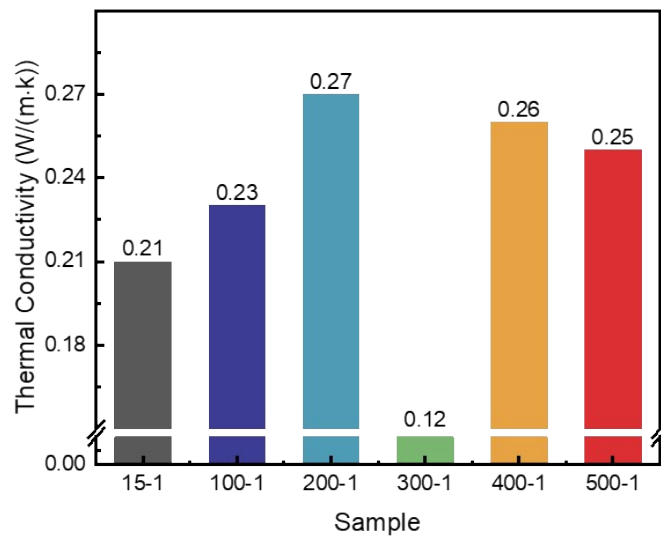


Figure S8. The thermal conductivity of PU-TA with different V_e .

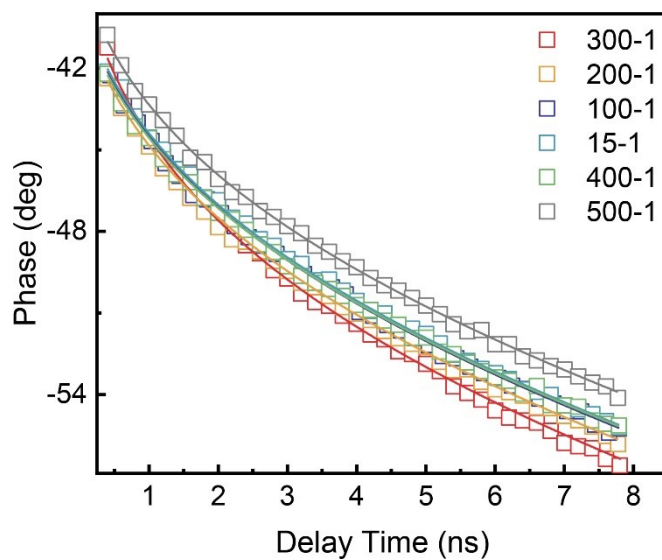


Figure S9. Phase signal and fitting curve of PU-TA with different V_e .

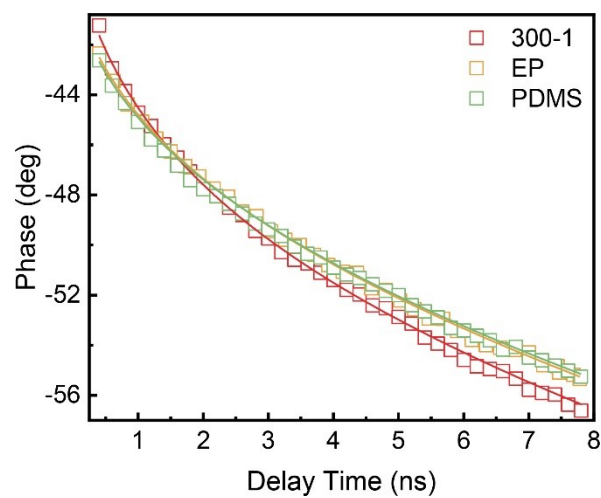


Figure S10. Phase signal and fitting curve of PU-TA@300-1, PDMS and EP.

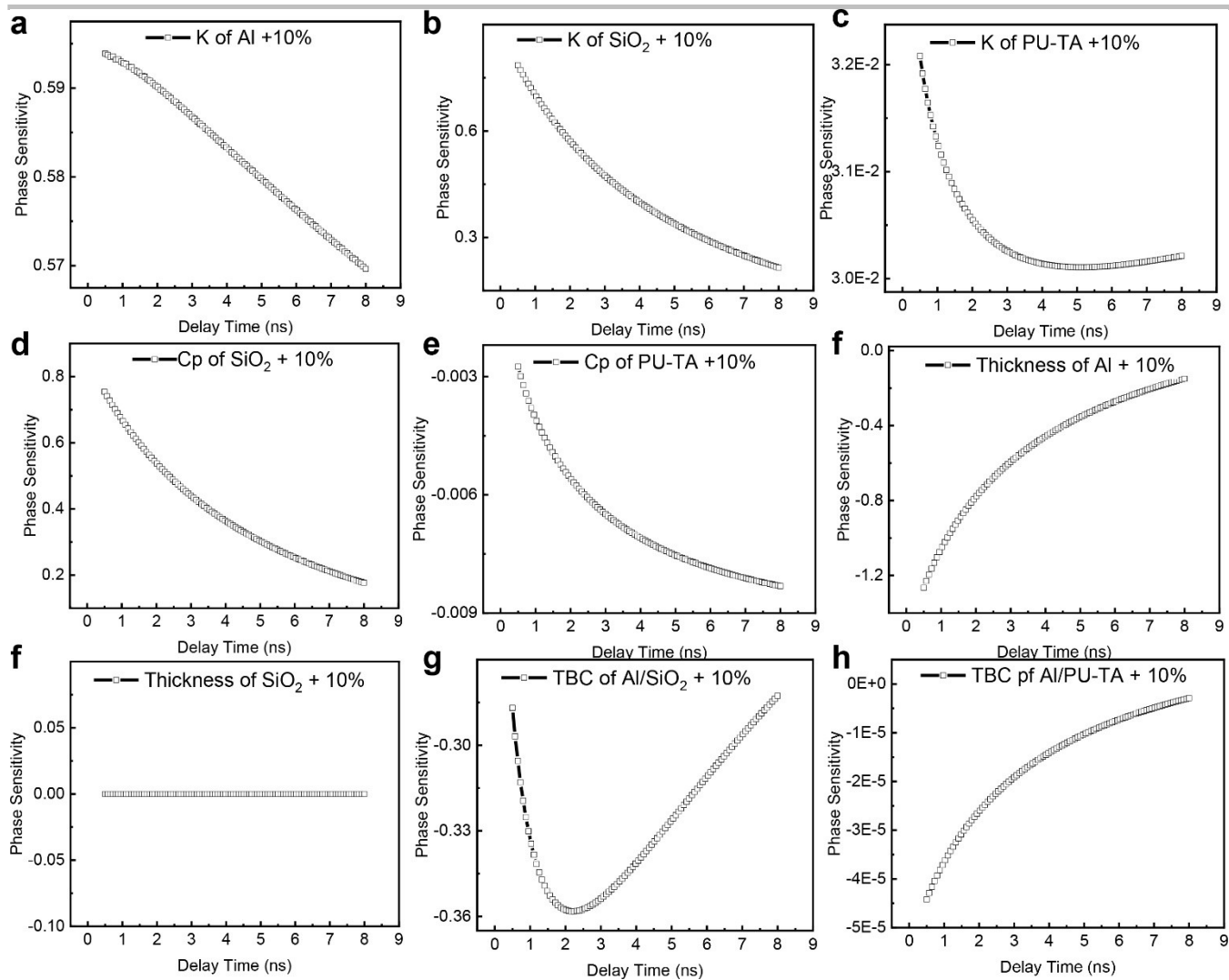


Figure S11. Sensitivity of different parameters. K represents thermal conductivity; Cp represents heat capacity.

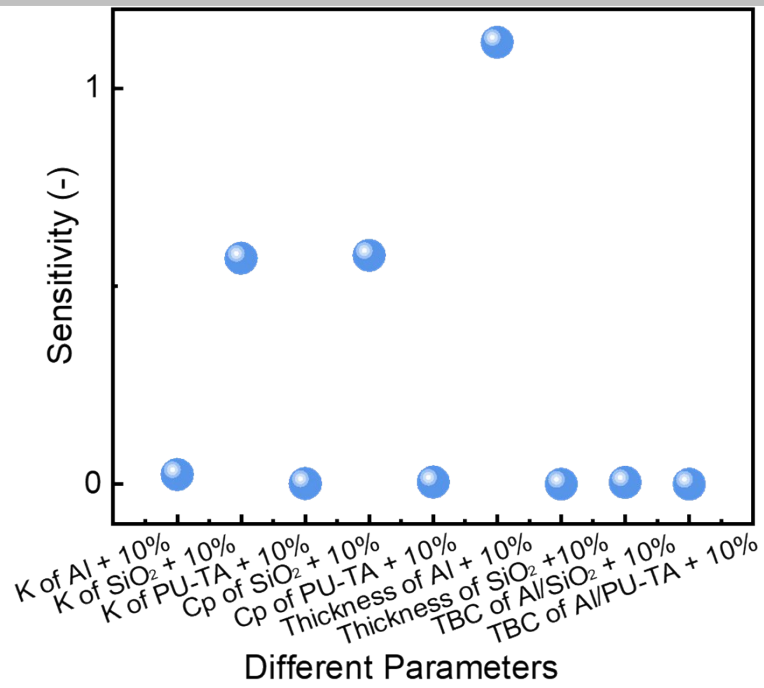


Figure S12. Differences of sensitivity between various factors.

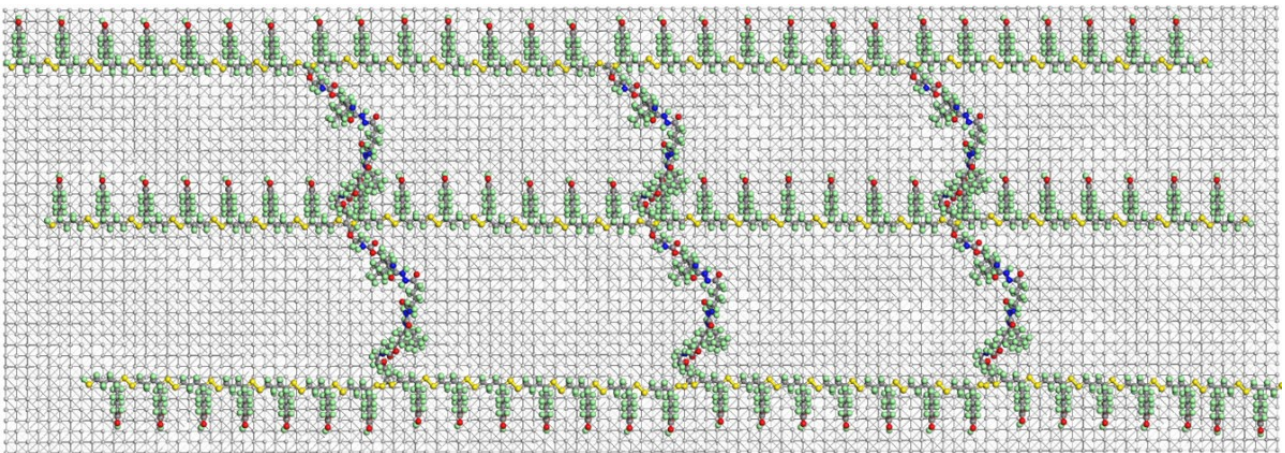


Figure S13. Schematic of PU-TA thermal interface model taking 400-1 as an example.

Table S1. Contact angles tested by three types of probe liquids.

| Contact angles | Diiodomethane | Ethylene glycol | Water |
|----------------|---------------|-----------------|-------|
| Al-1 | 60.3 | 87.2 | 66.3 |

| | | | |
|------|------|------|------|
| Al-2 | 55.6 | 87.1 | 63.1 |
| Al-3 | 56.0 | 87.5 | 65.7 |
| Al-4 | 56.0 | 86.6 | 64.0 |
| Al-5 | 58.8 | 87.9 | 63.4 |
| Al-6 | 57.3 | 86.9 | 65.7 |

Table S2. Surface energy components of the three probe liquids and the Al layers estimated from the contact angles in Table S5 using equation (4) to (6).

| Material | γ | γ^{LW} | γ^{AB} | γ^+ | γ^- |
|-----------------|----------|---------------|---------------|----------------|-------------|
| Diiodomethane | 50.8 | 50.8 | ≈ 0 | ≈ 0.01 | ≈ 0 |
| Ethylene glycol | 48.0 | 29.0 | 19.0 | 3.0 | 30.1 |
| Water | 72.8 | 21.8 | 51 | 25.5 | 25.5 |
| Al-1 | 25.0 | 25.0 | ≈ 0 | ≈ 0 | 89.6 |
| Al-2 | 26.8 | 26.8 | ≈ 0 | ≈ 0 | 104.0 |
| Al-3 | 25.3 | 25.3 | ≈ 0 | ≈ 0 | 103.4 |
| Al-4 | 26.3 | 26.3 | ≈ 0 | ≈ 0 | 101.6 |
| Al-5 | 26.6 | 26.6 | ≈ 0 | ≈ 0 | 95.9 |
| Al-6 | 25.3 | 25.3 | ≈ 0 | ≈ 0 | 98.1 |

Table S3. Roughness of PU-TA with various Ve

| Samples | Sa(um) | Sz(um) | Str | Spc | Sdr |
|---------|--------|--------|-------|---------|----------|
| 15-1 | 0.349 | 1.736 | 0.368 | 290.905 | 0.000128 |
| 100-1 | 0.343 | 1.954 | 0.471 | 608.054 | 0.000148 |
| 200-1 | 0.341 | 1.616 | 0.305 | 483.874 | 0.000172 |
| 300-1 | 0.336 | 1.514 | 0.305 | 280.195 | 0.000126 |
| 400-1 | 0.335 | 1.502 | 0.327 | 673.061 | 0.000181 |
| 500-1 | 0.337 | 1.425 | 0.302 | 217.408 | 0.000106 |

Table S4. Parameters used in multilayer thermal conduction model

| | Layer thickness | Thermal conductivity | Heat capacity |
|--------------|--------------------|----------------------|-------------------------------|
| Fused silica | 200 um | 1.30 W/(m·K) | 1.63e6 J/(m ³ ·K) |
| Al | 46 nm | 237.00 W/(m·K) | 2.42e6 J/(m ³ ·K) |
| PU-TA | -1 (semi-infinite) | 0.12-0.27 W/(m·K) | 2.17e6 J/(m ³ ·K) |
| PDMS | -1 (semi-infinite) | 0.29 W/(m·K) | 1.42e3 J/(m ³ ·K) |
| EP | -1 (semi-infinite) | 0.26 W/(m·K) | 1.27 e6 J/(m ³ ·K) |

Table S5. Nodes and monomers in PU-TA with different Ve

| Samples | Nodes | Monomers |
|---------|-------|----------|
| 15-1 | 1 | 11 |
| 100-1 | 12 | 5 |
| 200-1 | 10 | 5 |
| 300-1 | 11 | 5 |
| 400-1 | 6 | 7 |
| 500-1 | 6 | 8 |

Table S6. Energy and distance in lj/cut between different types of atoms

| i-j | $\epsilon_{i-j}/\text{kcal/mol}$ | $\sigma_{i-j}/\text{\AA}$ |
|-----|----------------------------------|---------------------------|
|-----|----------------------------------|---------------------------|

| | | |
|------|-------|-------|
| Al-C | 0.054 | 4.010 |
| Al-H | 0.020 | 2.995 |
| Al-O | 0.267 | 3.300 |
| Al-N | 0.106 | 4.070 |
| Al-S | 0.071 | 4.027 |
