Thermally Conductive and Compliant Polyurethane Elastomer Composites by Constructing Tri-branched Polymer Network

Hengyi Shi[a,b], Wei Zhou[a,*], Zhibin Wen [a,*], Weixuan Wang[c], Xiaoliang Zeng[a], Rong Sun[a], and Linlin Ren [a, *]

[a] Shenzhen Institute of Advanced Electronic Materials, Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China

[b] Shenzhen College of Advanced Technology, University of Chinese Academy of Sciences, Shenzhen 518055, China

[c] School of Energy and Power Engineering, Changsha University of Science and Technology, Changsha 410114, China.

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Experimental Procedures

1. Materials and Methods

1.1. Materials

Polytetrahydrofuran (PTMG), dibutyltin dilaurate (DBTDL), castor oil and isophorone diisocyanate were provided by Aladdin Holdings Group Co., Ltd, China. Aluminum powders were purchased from Anshan Iron and Steel Group Co., Ltd., China. Polydimethylsiloxane (PDMS) were supplied by Mingyi Silicone Group Co., Ltd., China. All materials were used as received.

1.2. Synthesis of the tri-branched prepolymer

Isophorone diisocyanate (13.34 g, 0.06 mol), and castor oil (18.67 g, 0.02 mol) were placed in a round-bottomed flask. The solution was heated to 80 °C and stirred for 3 h. After the reaction was accomplished, the liquid was cooled down to room temperature to obtain the tri-branched prepolymer (32.01g, 0.02 mol). It was a light yellow yet clear liquid, and it was storaged in refrigerato r.

1.3. Synthesis of the tetra-branched prepolymer

Pentaerythritol (2.04 g, 0.015 mol), isoflurone diisocyanate (13.34 g, 0.06 mol) and dibutyltin dilaurate (0.076 g, 0.5 wt%) as catalyst were placed in a round-bottomed flask. The mixture was dissolved in DMF (25 mL), and it was stirred and heated to 70 °C for 10 min. After the reaction was finished completedly, the solution was cooled down to room temperature to get the tetra-branched prepolymer (~39.09 g, 0.015 mol). It was a colourless clear solution, and it was storaged in refrigerator.

1.4. Synthesis of the tri-branched polyurethane elastomer composites

Tri-branched prepolymer (1.6 g, 1 mmol), polytetrahydrofuran (PTMG) (2.1 g, 1.05 mmol), hydroxyl polydimethylsiloxane (PDMS) (0.525 g, 0.3 mmol) and triethanolamine (TEA) (0.01 g, 0.1 mmol) were placed in a mixing tank (120 mL, FlackTek SpeedMixer), and mixed by a high-speed mixer (DAC 1400-1000, VAC FlackTek SpeedMixer). Aluminum powders were added by corresponding quality according to the required filler mass fraction, and then using the high-speed mixer to make the fillers will be dispersed in uncured elastomer well. Lastly, 0.5 wt% dibutyltin dilaurate as catalyst was added, and the mixture was mixed again by a high-speed mixer. The tri-branched polyurethane elastomer composites were obtained after three-stage curing (80 °C/2h, 120 °C/3h, 150 °C/3h).

1.5. Synthesis of the tetra-branched polyurethane elastomer composites

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2. Characterization methods.

2.1. Structural Characterization

ATR-FTIR spectra were recorded on a Thermo Scientific Nicolet 6700 FTIR spectrometer. Samples were scanned from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} for 64 scans. The molecular weights (Mn and Mw) and polydispersity index (PDI) of PU prepolymer (PUP) was measured by gel permeation chromatography (GPC, waters) calibrated with polystyrene standards. The flow rate of eluent (THF) was 1 mL/min, and the concentration of sample was ~5.0 mg/mL.

2.2. Mechanical Tests.

Tensile tests of elastomers were performed on a commercial tensile tester, the tested specimens were cut into a dumbbell shape with an initial length of 25 mm and a width of 2 mm. All tests were repeated at least three times.

2.3. Young's Modulus.

The Young's modulus of elastomers is linearly fitted by the tensile curve within the strain range from 0% to 20%.

2.4. Rheological Test.

The rheological behaviors of elastomers were analyzed using a rheometer (Anton Paar MCR302). The disc-shaped elastomers specimens with thickness of ～1.5 mm and diameter of 25 mm. Frequency sweeps were performed on the samples at different temperatures and different filler contents with a strain of 0.03% (frequency range is 0.01-100 rad s^{-1}). The viscosity test used uncured elastomer with thickness of 1mm, diameter of 25mm, shear rate is from 0.01-10 s^{-1}.

2.5. Thermal conductivity Tests.

Thermal conductivity of the polyurethane elastomer composites was tested by a thermal constant analyzer (Hot-disk, TPS2500S).

The thermal conductivity of elastomers was tested by Hot-disk, and thermal resistance of elastomers was determined by LONGWIN TIM LW 9389. During the thermal conductivity test, elastomers clamp the probe in the middle, obtains the instantaneous heat flow after short heating, and obtains the thermal conductivity through fitting. In the thermal resistance test, the sample before curing was directly coated on the thermal conductivity meter, and the data were obtained at a pressure of 40 psi, the temperature of thermal resistance test was set to heat up to 80 ℃.

The temperature dependence of the thermal conductivity was measured by a flash thermal conductivity meter (LFA467) with the sample size of 10 mm (length) ×10 mm (width)×1.4 mm (thickness). The thermal conductivity of the elastomer composites is calculated through the Eq. S1:

$$\lambda = \alpha \times C_p \times \rho \#(S1)$$

where α is the thermal diffusivity, Cp is the specific heat capacity, and ρ is the density. The specific heat capacity was obtained by differential scanning calorimetry (DSC), and the density was measured by automatic density analyzer (ULTRAPYC 1200E).
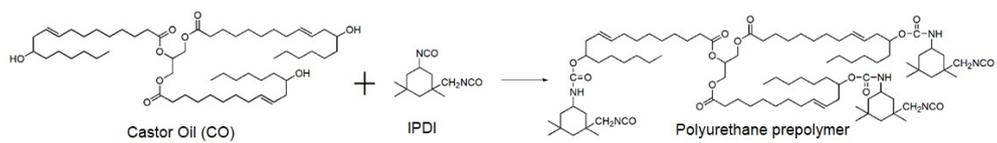
Fig. S1 Synthesis of trifunctional crosslinking point
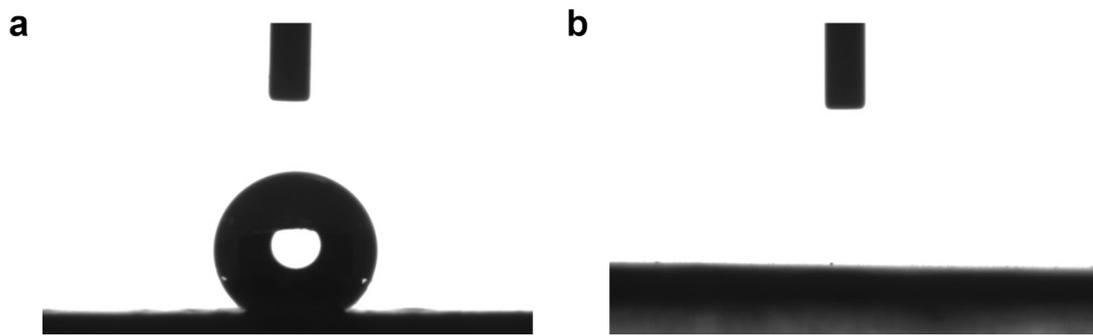
Fig. S2 Water contact angle of a. modified fillers and b. unmodified fillers.
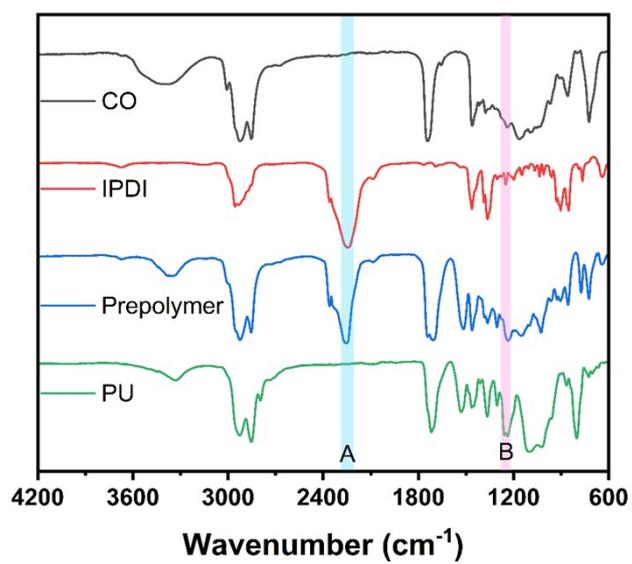
Fig. S3 FTIR of CO, IPDI, Prepolymer and PU.
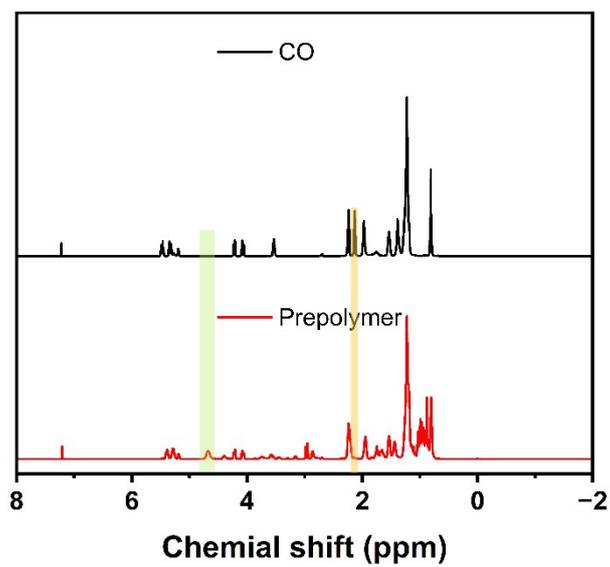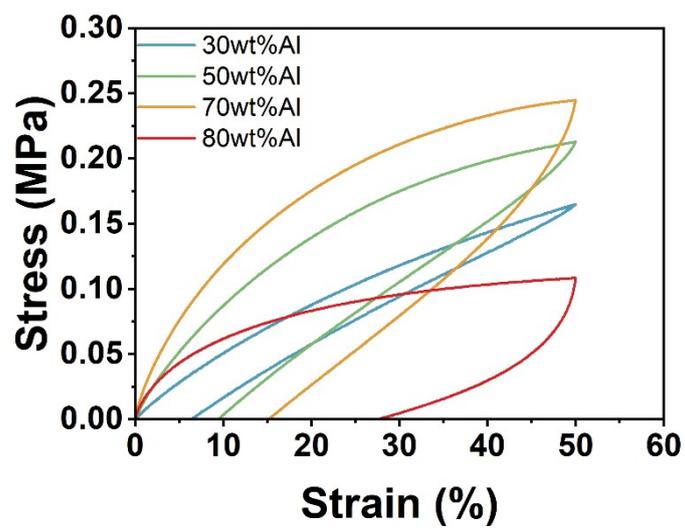
Fig. S4 ^{1}HNMR spectra of CO and Prepolymer.
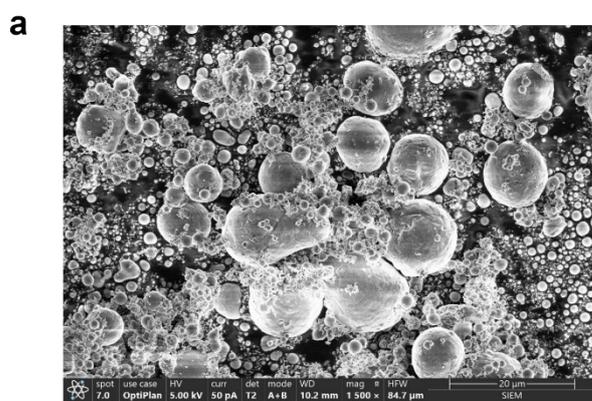
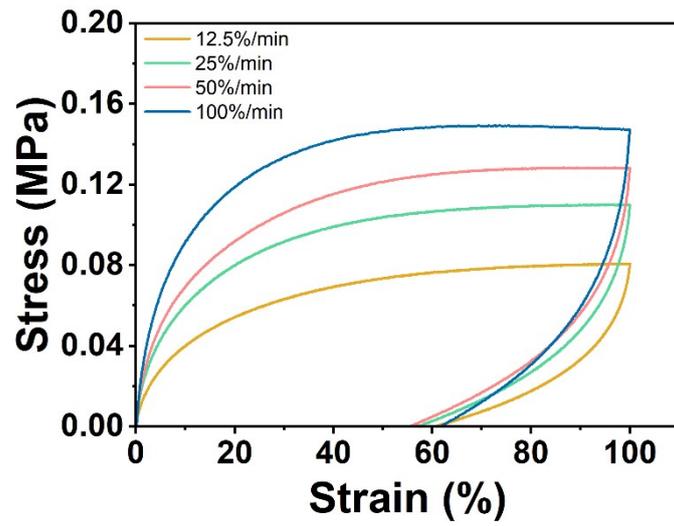**Fig. S5** SEM images. (a). Fillers, (b) Polyurethane elastomer composite.
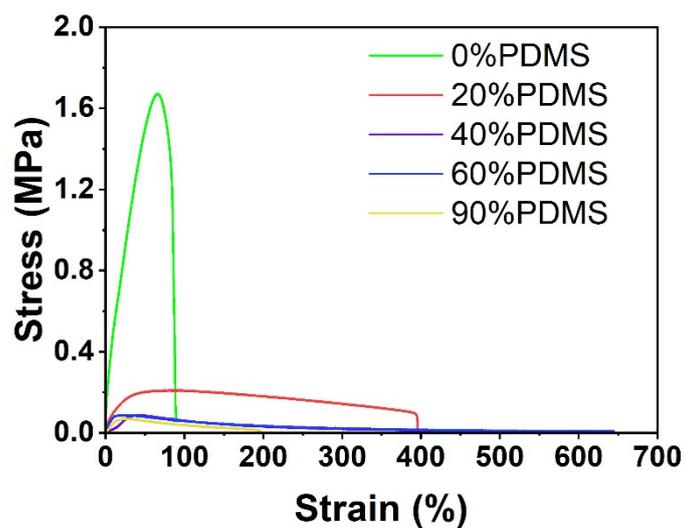
Fig. S6 Stress-strain curves of the tri-branched polyurethane elastomer composites with 91 wt% Al with different percentage of PDMS at a loading rate of 20 mm/min.
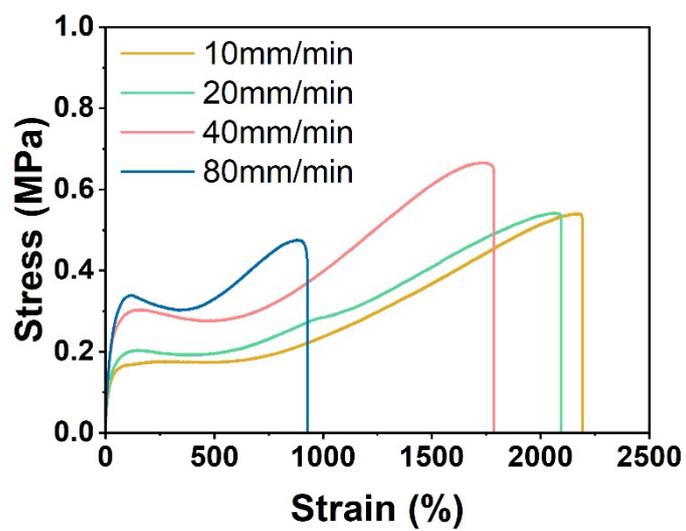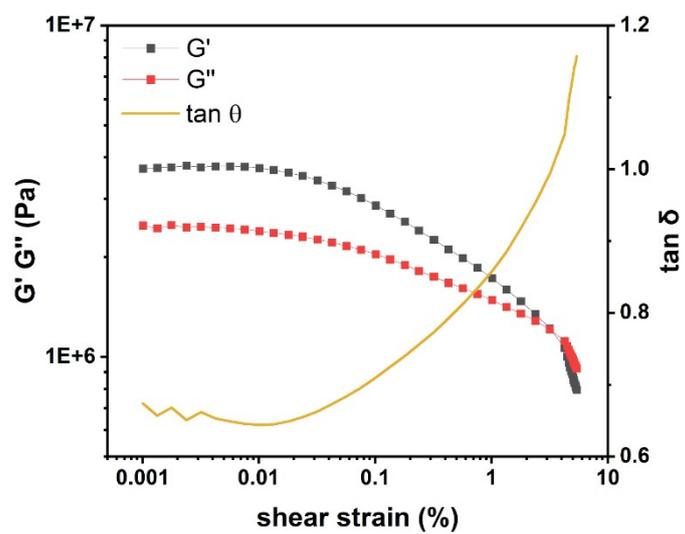
Fig. S7 Stress-strain curves of the tri-branched polyurethane elastomer composites
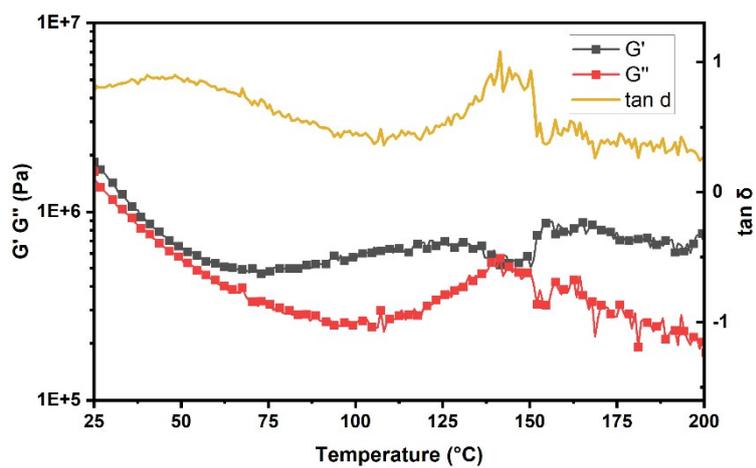
with 80 wt% Al at different loading rate.

Fig. S8 Cyclic stress-strain curves of the tri-branched polyurethane elastomer composites with different filler contents at a loading speed of 25%/min.

Fig. S9 Cyclic stress-strain curves of the tri-branched polyurethane elastomer composites with 80wt% Al at different loading rate.

**Fig. S10** Strain dependence of storage modulus (G′), loss modulus (G″) and loss factor (tan θ) of the tri-branched polyurethane elastomer.

Fig. S11 Temperature dependence of storage modulus (G′), loss modulus (G″) and

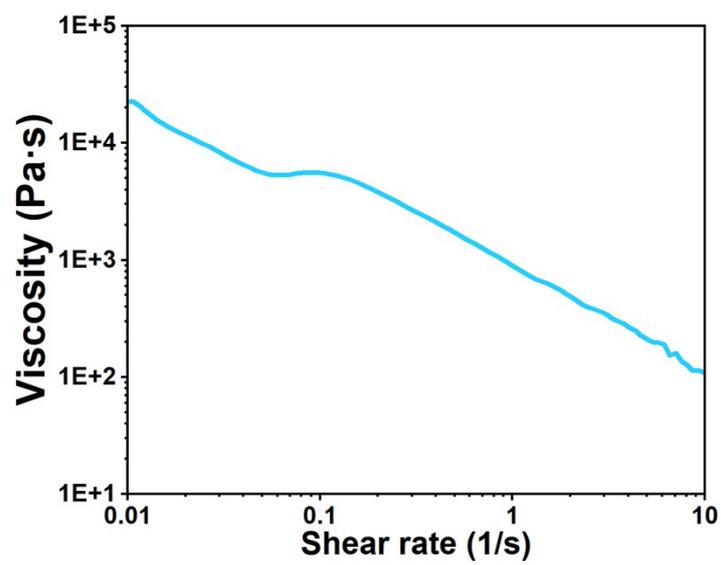loss factor (tan θ) of the tri-branched polyurethane elastomer composites.
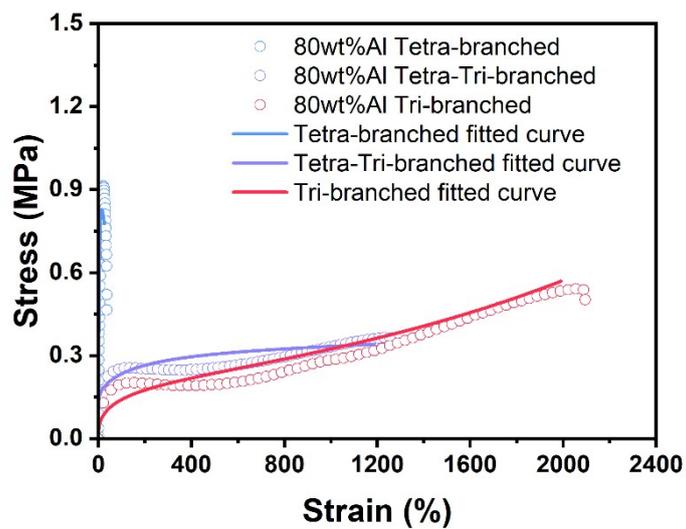
Fig. S12 Stress-strain curves fitted by viscoelastic models of the different branched polyurethane elastomer composites with 80wt% Al.
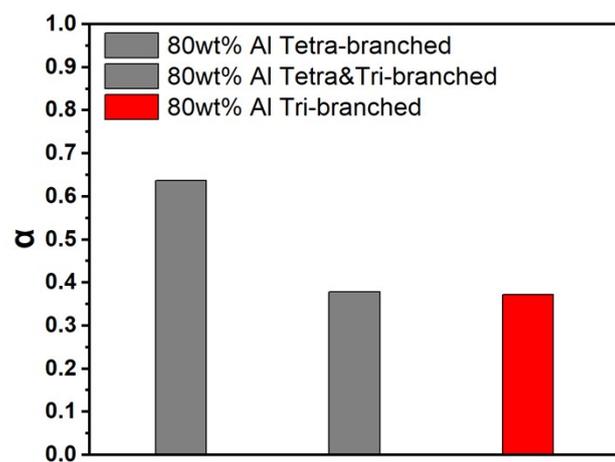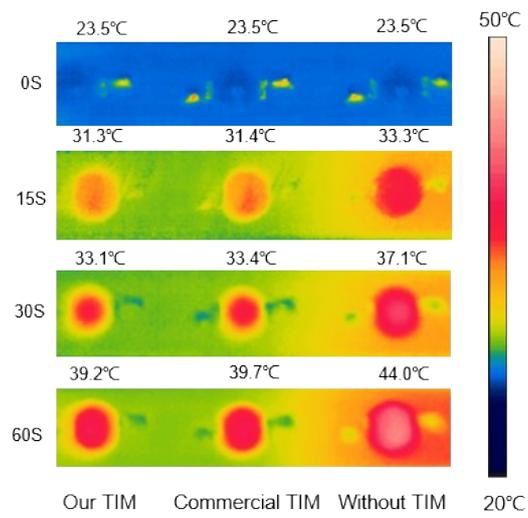
Fig. S13 The number of α corresponding to different branching networks.
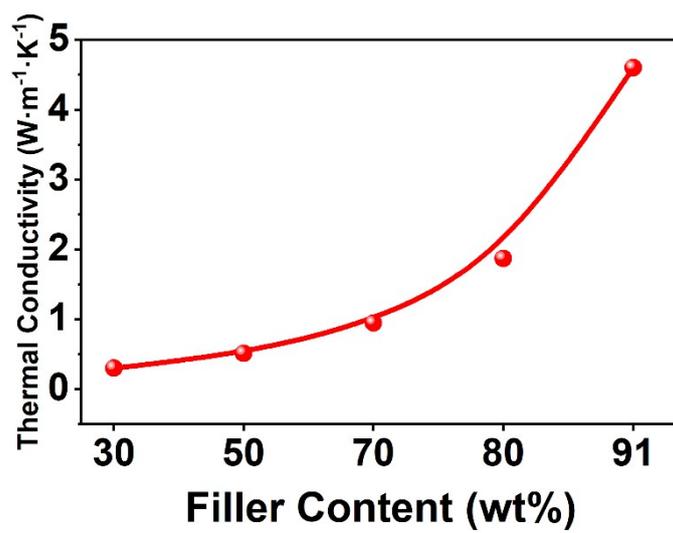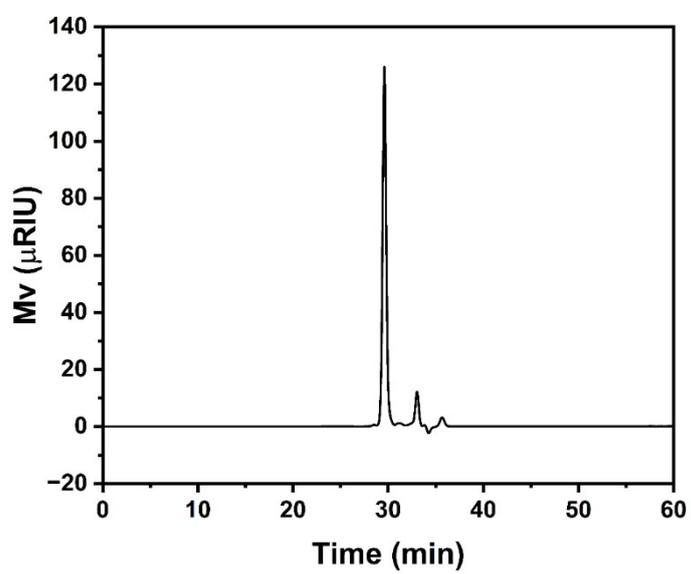
Fig. S14 Thermal conductivity of the tri-branched polyurethane elastomer composites with different filler content.

Fig. S15 The viscosity of the uncured tri-branched polyurethane elastomer composite.

Fig. S16 Heat dissipation effect of different TIMs in LED light strip.

Fig. S17 GPC curve of castor oil.

Table S1 Fitting parameters and the density of polymer matrix of the different branched polyurethane elastomer composites with 80wt% Al.

Elastomer	G_e (MPa)	λ_m	ρ
Tetra-branched	5	1.25	0.985
Tetra-Tri-branched	36	13.65	0.990
Tri-branched	58	22.00	0.995

Table S2. The GPC results of castor oil

Sample	Mw	Mn	PDI
Castor oil	1498	1462	1.02