Electronic Supplementary Information (ESI)

A Fully Polydicyclopentadien Skeletonized Epoxy Resin System and their Fundamental Properties as Electronic Materials

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Experimental

Materials. Dicyclopentadiene (DCPD), phenol, epichlorohydrin, cysteamine, $BF_3{\cdot}O(C_2H_5)_2$, diethylenetriamine, tris(dibenzylideneacetone) dipalladium (0), silver hexafluoroantimonate, 4.4'-Azobis (4-cyanovaleric acid) (ABV), tetramethylammonium bromide (TMAB), diethylenetriamine (DTA) and deuterated solvents for NMR test were purchased from Aladdin Reagents. Toluene, tetrahydrofuran (THF), NaOH and ethanol were obtained from Sinopharm Chemical Reagent. Water is Millipore grade. DCPD was washed with 5 wt % Na_2CO_3 aqueous solution to remove inhibitor and dried using magnesium sulfate. Diglycidyl ether of bisphenol-A (DGEBA, E-51, epoxy equivalent weight (EEW) = 196 g / mol) commercial epoxy product was received from Shanghai Autun Chemical Tech. Co. Ltd.

Synthesis of DCPDDE. In the first step, to a 500 ml flask, 8.0 mol of phenol and 100 mL of toluene containing 0.5 wt % $BF_3.Et_2O$ were added and heated to 70 °C under magnetic stirring; 1 mol of DCPD was then introduced dropwise over 1 h under N_2 protection. Afterward, this mixture was heated at 110-120 °C for 4 h. After cooling down to room temperature, the solution was washed with 5 wt % aqueous Na_2CO_3 solution and deionized water three times. The organic phase was collected and concentrated to remove the toluene and excess phenol using rotary evaporator to achieve the DCPD-phenol product with a yield of ~ 92%.

In the second step, 32 g of DCPD-phenol and 78.2 mL of epichlorohydrin were mixed in a 500 ml flask. Under stirring, 3.08 g of TMAB was added to this solution, and heated at 75 °C for 2 h for polymer chain propagation; then this solution was cooled to 65 °C, followed by adding 192 mL of 48 wt% NaOH aqueous solution over a period of 1 h at 65 °C for another 1 h. After cooling, the organic phase was separated and washed with water for three times. Finally, excess epichlorohydrin was distilled to leave the final DCPDDE product with a yield of ~ 88 % (viscosity = 3,500 mPa·S@23 °C, molecular weight (M_n) = ~1314, polydispersity index (PDI) = ~ 1.2, measured by Gel Permeation Chromatography (GPC), EEW = 220 g / mol). Another DCPDDE sample with M_n = ~ 8610 and viscosity = 12,600 mPa·S@23 °C was also synthesized by simply extending the chain propagation time to 6 h, with the presence TMAB catalyst at 75 °C.

Synthesis of PDCPDAm. Firstly, to a 250 mL round-bottom flask, 100 mL of toluene, 13 mg of $[PdCl(C_3H_5)]_2$, 30 mg of $AgSbF_6$ and 45 g of DCPD were mixed and heated at 70 °C under N_2 protection. This solution was kept at 70 °C for 24 h to perform the polymerization. After cooling to room temperature, 30 g of silica-gel powder was introduced to the solution and mixed for 12 h to adsorb and recycle the Pd / Ag catalyst. After filtration to separate the silica, the solution was poured in 500 mL of methanol and mixed for 30 min to obtain white polymer deposit of PDCPD. The polymer product was collected and washed with methanol on a filter paper, and then dried under vacuum at room temperature (yield = ~ 83 %, M_n = ~ 2100, PDI = ~ 1.8).

Secondly, 10 g of PDCPD was dissolved in 60 mL of THF and mixed with 0.2 g of ABV under N_2 protection; to this solution, 15 mL of aqueous solution containing 17 g of cysteamine was added. This mixture was stirred vigorously and heated at 60 °C for 6 h. After cooling to room temperature, the polymer was separated using 500 mL of methanol (yield = ~ 86 %) to obtain the PDCPDAm curing agent.

Curing of epoxy resins. DCPDDE epoxy were mixed with PDCPDAm curing agent at different ratios and heated at 120 °C for 2 h and post-cured at 180 °C for another 1 h. DGEBA resin with DTA or PDCPDAm curing agent are cured at 100 °C for 2 h.

Characterization. IR spectra were collected with a *Nicolet* iS50 IR spectrometer. A JEOL-7800F SEM was used to image the sample morphology. A Bruker Avance II 400MHz NMR spectrometer were applied to obtain the ^{1}H-NMR spectra. Molecular weight of polymers was measured using Shimazu LC-20A GPC. TG and TMA were tested using a NETZSCH STA449 F5 and TMA 402 F3, respectively. Bonding test (pull-off adhesion test) was conducted using an SH-M Pull-off testing set (Fig. S3) based on ADTM D4541 standard. Tensile and elongation test were performed based on ASTM D412-C standard. A Keysight® Tech. DPS 50 system was used to measure the D_k and D_f of the samples based on IPC-TM-650 and ASTM 3380 standards.

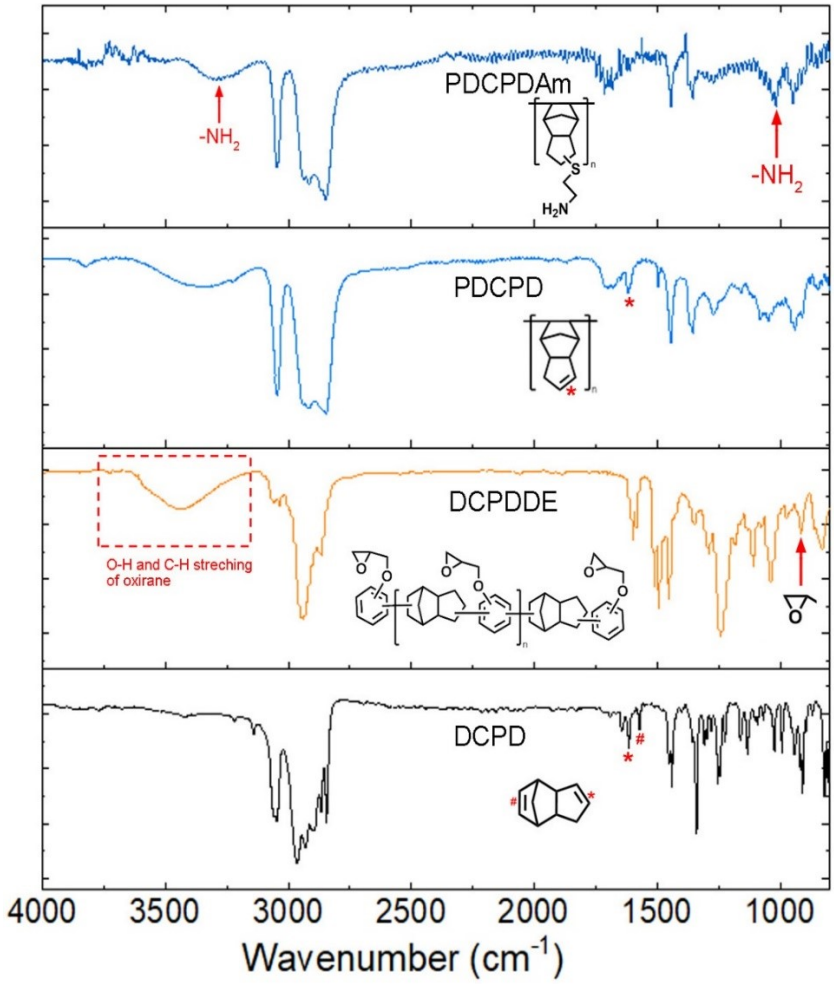

Fig. S1. IR spectra of DCPD, DCPDDE, PDCPD and PDCPEAm.

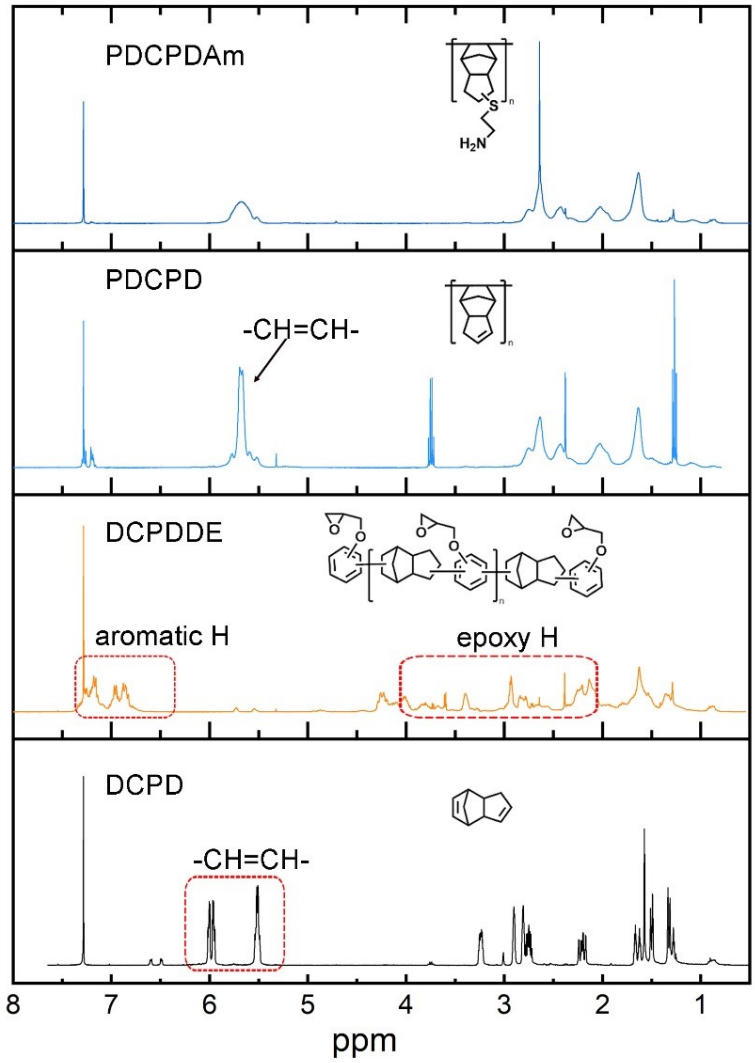

Fig. S2. ^{1}H-NMR spectra of DCPD, DCPDDE, PDCPD and PDCPDAm.

Table S1. Mechanical properties of the epoxy resins.

Epoxy resin : Curing agent (Mass Ratio)	DCPDDE : PDCPDAm			DGEBA : PDCPDAm			DGEBA : DTA		
	Hardness (Shore D)	Tensile strength (MPa)	Elongation (%)	Hardness (Shore D)	Tensile strength (MPa)	Elongation (%)	Hardness (Shore D)	Tensile strength (MPa)	Elongation (%)
100 : 10	64	67.7	13.4	60	61.6	15.5	53	58.3	17.7
100 : 20	66	69.5	12.8	61	65.3	15.2	57	60.6	15.3
100 : 30	71	79.2	11.5	63	68.8	14.3	61	62.4	12.4
100 : 40	76	82.5	9.4	65	72.5	13.1	62	63.8	12.2
100 : 50	79	83.4	8.6	66	73.6	12.8	63	64.2	11.6

Table S2. Major thermo, mechanic and dielectric properties of the PDCPDDE-Am resin using DCPDDE of M_n = ~ 8610.

DCPDDE : PDCPDAm (Mass Ratio)	T_g (°C)	Hardness (Shore D)	Tensile strength (MPa)	D_k / D_f (10 GHz)
100 : 10	154.2	66	69.4	2.68 / 0.0069
100 : 30	228.5	74	74.5	2.66 / 0.0065
100 : 50	273.6	82	86.1	2.64 / 0.0065

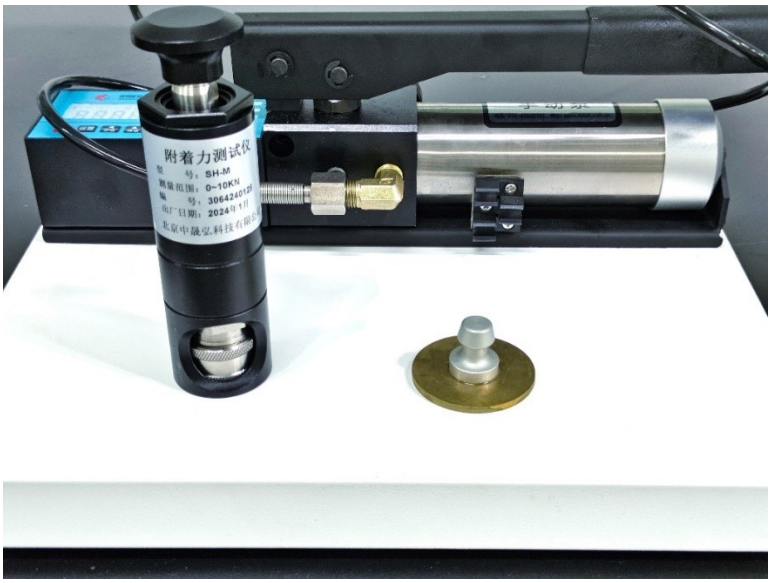

Fig. S3. Bonding test of epoxy with Cu.