

Supplementary Material

Enhancing the mechanical strength and toughness of epoxy resins with linear POSS nano modifiers

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Materials

Diglycidyl ether resin (DER332) with an epoxy equivalent weight (the weight of resin containing 1 equiv of epoxy functional group) of 171–175 g per equivalent was purchased from Dow Chemicals (USA). 9,9-Bis(4-hydroxyphenyl)fluorene (98%) was provided by TCI. A mixture (denoted as LC100) of 3,5-diethyltoluene-2,4-diamine (75–81 wt%), and 3,5-diethyltoluene-2,6-diamine (18–20 wt%) was purchased from Ethacure. Allyl glycidyl ether (99%), dichloromethylsilane (99%), Pt(dvs),

tetrabutylammoniumbromide (TBAB), triethylamine (99%) and trimethoxyphenylsilane (98%) were from Sigma-Aldrich. All solvents were of AR grade. Isopropanol (IPA), tetrahydrofuran (THF) and methanol were provided by J. T. Baker. THF and toluene was distilled before use.

Synthesis of diglycidyloxypropyl POSS (G-POSS)

In a typical reaction, phenyltrimethoxysilane (242 mmol, 48.0 g) was added dropwise to a mixture of sodium hydroxide (160 mmol, 6.4 g), water (278 mmol, 5.0 g) and 2-propanol (240 mL). The mixture was stirred for 4 h with refluxing, and then left at room temperature for one day. The precipitate was filtered and washed with IPA followed by drying in vacuum at 70 °C for 5 h. A mixture of this precipitate (11.6 g), triethylamine (30 mmol, 3.0 g) and THF (100 mL) were added to a 250 mL flask and put into an ice-water bath. After cooling down, dichloromethylsilane (30 mmol, 3.4 g) was added dropwise. The mixture was then stirred at room temperature for 12 h. After removing the precipitate by centrifuge, the filtrate was evaporated to give white solid. The solid was washed with methanol to give 3,13-dihydrooctaphenyl POSS (7.1 g, yield 20 %). ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.55-7.16 (m, 40H). 4.97 (q, 2H), 0.36 (d, 6H), ¹³C NMR (100 MHz, CDCl₃, δ ppm): 134.47, 134.34, 131.24, 132.02, 131.18, 131.12, 130.88, 130.81, 128.23, 128.05, 1.03, ²⁹Si-NMR (80 MHz, CDCl₃, δ ppm): 79.3, 79.1, 77.8, 32.8.

6.0 g of 3,13-dihydrooctaphenyl POSS product prepared above was placed inside a 100 mL flask and added with allyl glycidyl ether (2.5 g) and anhydrous THF (50 mL). The system was purged for half an hour using highly pure argon and then 3 drops of Pt(dvs) was added. The mixture was then reflux at 65 °C for 36 h to ensure that

hydrosilylation was completed. The solvent and excess allyl glycidyl ether was removed under reduced pressure to afford the diglycidyloxypropyl POSS solids (denoted as G-POSS in Scheme 1) with the yield of 95%. ¹H NMR (ppm, CDCl₃): 0.30 (s, 3H), 0.747 (t, 2H), 1.69 (m, 2H), 2.45 and 2.66 (m, 2H) 2.97 (m, 1H), 3.17 and 3.47 (m, 2H), 3.34 (m, 2H). MALDI-TOF (Product + Na⁺): 1404.2 Da (calculated: 1403.2 Da).

Methods

NMR measurements were carried out on a Bruker 400 NMR spectrometer. MALDI-TOF-MS experiment was carried out on an Autoflex III TOF/TOF equipped with a smart beam pulsed nitrogen laser ($\lambda = 337$ nm; pulse width = 3 ns). Dihydroxybenzoic acid was used as the matrix with THF as the solvent. Molecular weights were estimated by Gel permeation chromatography (GPC) on a Waters 2690 Separations Module with a Waters 410 Differential Refractometer. HPLC grade THF was used as the eluent at a flow rate of 1.0 mL/min, and the column system was calibrated by standard polystyrene in THF. Thermal gravimetric analysis (TGA) was performed on a TA Instruments Q500 thermal gravimetric analyzer. Measurements were conducted in nitrogen atmosphere from ambient temperature to 700 °C with a heating rate of 20 °C/min. Differential scanning calorimetric (DSC) measurements were performed on a TA Instruments Q100 Calorimeter. A heating rate of 20 °C/min was used. Glass transition temperature (T_g) was taken as the midpoint of the heat capacity change as identified by the change in the slopes. TA Instruments DMA Q800 dynamic mechanical analyzer (DMA) was used to evaluate the viscoelastic mechanical performance of the polymer under dynamic loadings. The frequency was set to 1Hz and temperature ramped at 3.00 °C/min from room temperature to

240 °C. The T_g was determined from the peak of the Tan delta versus temperature plot. ASTM D 638 was applied. JEOL JSM-7600F FESEM was used to examine the fracture surface of the polymer after the tensile test. JEOL-2100 TEM was used to observe the morphology of the doped hybrid polymers. The samples were cut using a Lecia Ultracut UCT ultramicrotome and placed on carbon coated copper grids.

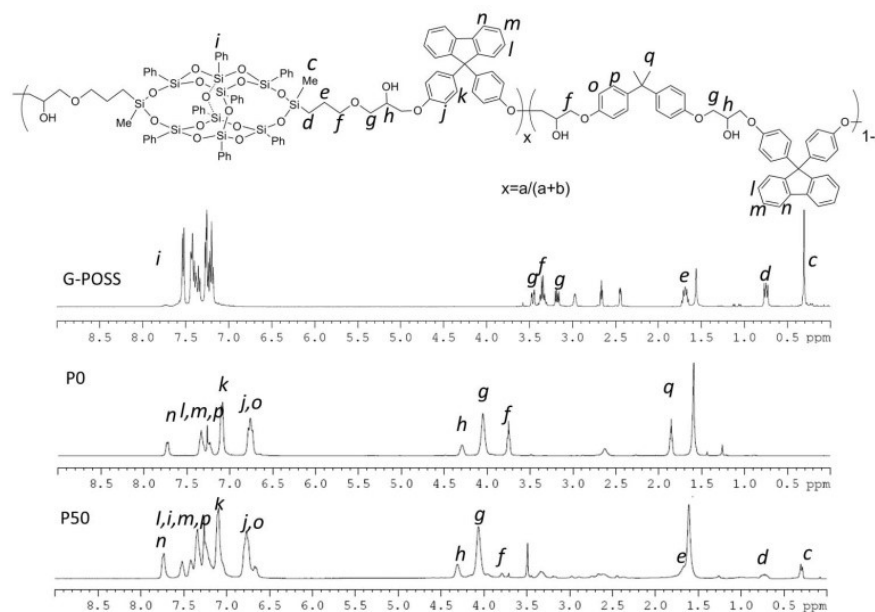


Figure S1. Typical ^1H -NMR spectra of G-POSS, P0 and P50.

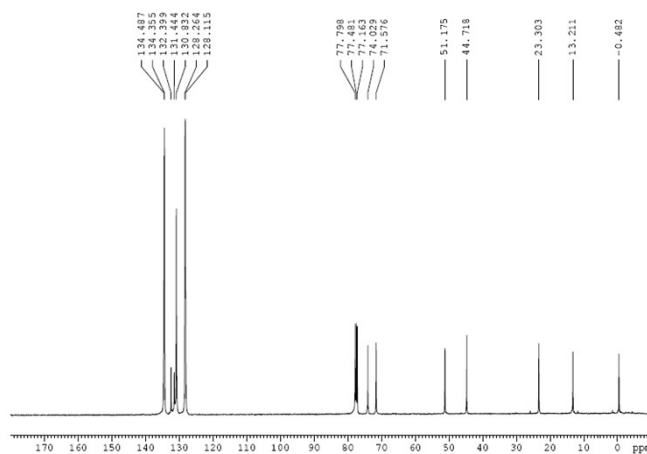


Figure S2. ^{13}C -NMR of G-POSS.

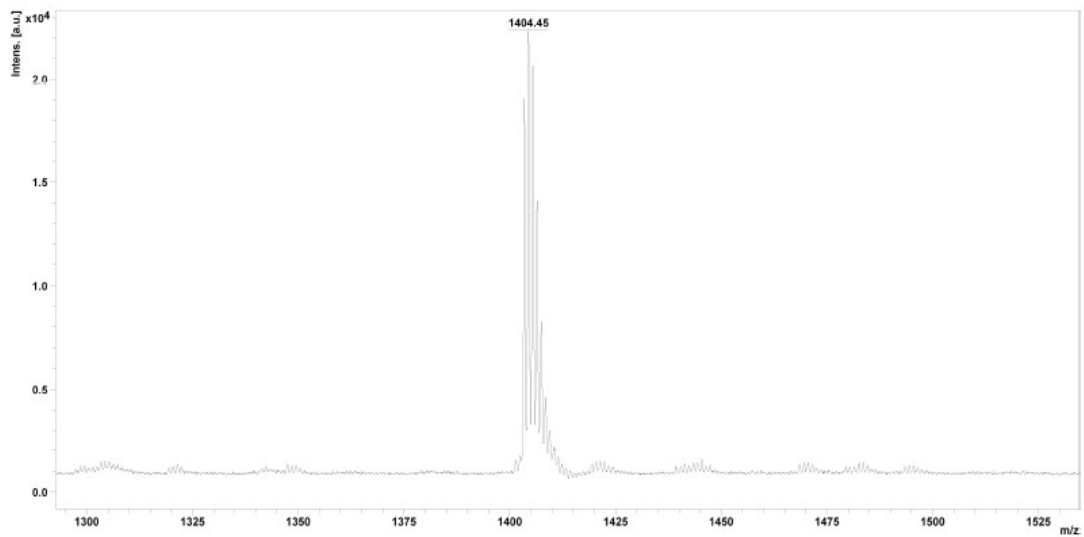
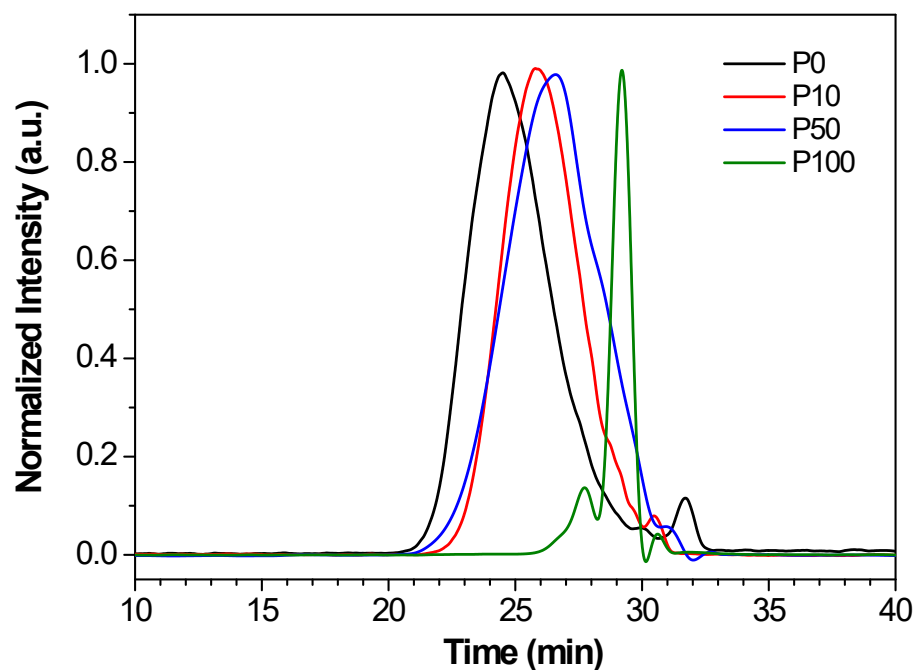


Figure S3. Mw of G-POSS+Na⁺ from MALDI-TOF.



GPC Results (P0)

	Mn	Mw	MP	Mz	Mz+1	Polydispersity	Retention Time (min)
1	15316	31235	28150	55540	89931	2.039409	24.445

GPC Results (P10)

	Mn	Mw	MP	Mz	Mz+1	Polydispersity	Retention Time (min)
1	8086	15488	13251	25214	37135	1.915362	25.889

GPC Results (P50)

	Mn	Mw	MP	Mz	Mz+1	Polydispersity	Retention Time (min)
1	8710	16200	12934	26662	40017	1.859927	25.937

GPC Results (P100)

	Mn	Mw	MP	Mz	Mz+1	Polydispersity	Retention Time (min)
1	2447	2872	2590	3650	4931	1.173287	28.998

Table S1. The molecular weight and polydispersity of the resultant nano modifiers.