Electronic Supplementary Material (ESI) for Chemical Communications

A thermally healable polyhedral oligomeric silsesquioxane (POSS) nanocomposite based on Diels-Alder chemistry

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Electronic Supplementary Information

Experimental details

Materials

Glycidyl POSS (G-POSS) was purchased from Hybrid Plastics Co. Furfurylamine (FA) (99.9%), 1,1′-(methylenedi-4,1-phenylene)bismaleimide (MPBMI) (95%), anhydrous tetrahydrofuran (THF) and dichloromethane were obtained from Sigma-Aldrich.

Synthesis of furfuryl-functionalized G-POSS (FG-POSS)

FG-POSS was synthesized by reacting G-POSS with furfurylamine. Typically, 12.1 g G-POSS (9.0 mmol, 72.0 mmol epoxy group) was dissolved in 60 ml DMF in a three-neck round-bottom flask under stirring. The flask was then filled with dried nitrogen, and 8.7 g furfurylamine (89.7 mmol amide group) was added dropwise into the solution. After reaction at 60 ℃ for 22 hours, the unreacted furfurylamine and redundant solvent were removed using rotary evaporation and a viscous transparent liquid was obtained. The product was characterized by NMR. The ^{1}H NMR spectroscopy (DMSO-d_6, ppm): δ 0.55 (–SiCH_2CH$_2$–, 2H); 1.50 (–CH$_2$CH_2CH$_2$–, 2H); 3.20-3.45 (–CH$_2$CH_2O–, 2H); 3.20-3.45, 3.60-3.75 (–OCH_2CH(OH)–, 2H); 3.60-3.75 (–CH$_2$CH(OH)CH$_2$–, 1H); 3.30-3.45 (–CH(OH)CH_2NH–, 2H); 3.30-3.45 (–NHCH_2C–, 2H); 6.10-6.40 (*i*,*j*–H of furan, 2H); 7.55 (*h*–H of furan, 1H).

Preparation of self-healing POSS

The self-healing POSS was prepared by dissolving 5 g FG-POSS in 40 ml anhydrous THF, followed by the addition of a stoichiometric amount of MPBMI. After stirring at room temperature for 3 hours, the THF was slowly removed by rotary evaporation. The resultant viscous liquid was poured into a mould and kept at room temperature for 20 hours, 45 ℃ for 5 hours and 95 ℃ for 18 hours to obtain a transparent solid block.

Characterizations

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a JEOL 400 MHz NMR spectrometer with tetramethylsilane as the internal reference. FG-POSS and DA adduct samples were dissolved with deuterated DMSO. The time dependence of the DA reaction was monitored using NMR spectroscopy. Transmission electron microscopy (TEM) images were obtained using a JEOL 3000F high-resolution TEM at an accelerating voltage of 300 kV. Fourier transform infrared (FTIR) spectra were recorded using a Bruker Vertex70 spectrometer with a resolution of 4 cm^{-1} accumulating 32 scans. A Varian Cary 3 UV-Visible spectrometer was used to monitor the reaction process and kinetics. The FG-POSS and MPBMI were dissolved in dichloromethane. After being mixed, coated on a quartz slide and dried with nitrogen gas flow, the UV-visible spectra were recorded immediately and then every 30 minutes. Differential scanning calorimetry (DSC) curves were recorded on a TA Q200 differential scanning calorimeter in a dry nitrogen atmosphere. The heating rate was 20 ℃/min. Dynamic mechanical analysis (DMA) was conducted on a TA Q800 dynamic mechanical thermal analyser in a single cantilever mode. The temperature sweep tests were carried out from 38 ℃ to 135 ℃ at a heating rate of 1 ℃/min. The oscillating amplitude was 15 μm. The specimen dimension was $25\times4.6\times2.0$ mm^3.

Fig. S1 ^{1}H NMR spectrum of FG-POSS.

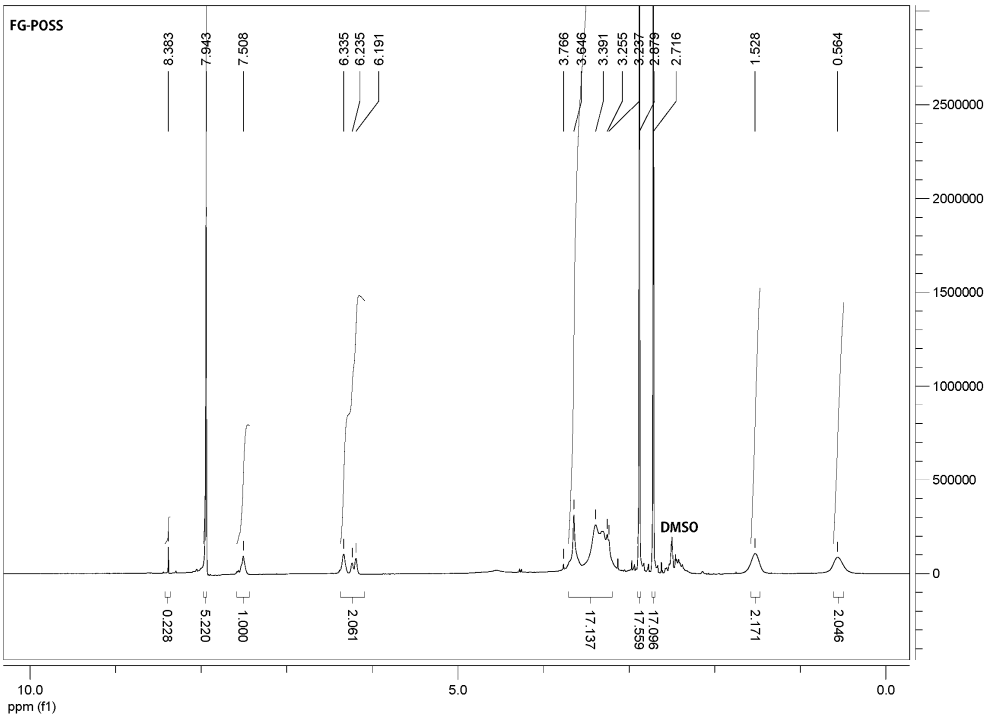

Fig. S2 Enlarged graph of Fig. 2b.