Supplementary Information

Enhancement of Thermomechanical Properties of Sulfur-rich Polymers by Post-Thermal Treatment

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Figure S1. Synthesis process of poly(sulfur-random-divinylbenzene) (poly(S₇₀-r-DVB₃₀)).



Figure S2. TGA thermograms of neat $poly(S_{70}-r-DVB_{30})$ and $poly(S_{70}-r-DVB_{30})$ thermally treated at 140 °C for 12, 24, and 48 h.



Figure S3. EDX data on the surface of neat $poly(S_{70}-r-DVB_{30})$ and $poly(S_{70}-r-DVB_{30})$ thermally treated at 140 °C for 12, 24, and 48 h.



Figure S4. Digital images of a) $poly(S_{70}-r-DVB_{30})$ chunk, b) $poly(S_{70}-r-DVB_{30})$ powder before thermal treatment, c) $poly(S_{70}-r-DVB_{30})$ film before thermal treatment, d) $poly(S_{70}-r-DVB_{30})$ powder after thermal treatment. Scale bars, 1 cm.



Figure S5. FT-IR transmittance data according to position in one poly(S₇₀-*r*-DVB₃₀) film.



Figure S6. Digital image of thermally degraded material during thermal treatment.



Figure S7. Carbon, hydrogen, and sulfur content of neat poly(S₇₀-*r*-DVB₃₀) and poly(S₇₀-*r*-DVB₃₀) thermally treated at 140 °C.



Figure S8. Deconvolution of FT-IR spectra of $poly(S_{70}-r-DVB_{30})$ films thermally treated at 110 °C for different treatment times: a) No thermally treated, b) 2 h, c) 12 h, d) 48 h.



Figure S9. Deconvolution of FT-IR spectra of $poly(S_{70}-r-DVB_{30})$ films thermally treated at 140 °C, 170 °C for each treatment time.



Figure S10. FT-IR transmittance spectra of a) thermal treatment at 110 °C, b) 140 °C, c) 170 °C from 3400 to 2000 cm⁻¹. The average thickness of films is 164 μ m. d) The transmittance at 4 μ m of annealed poly(S₇₀-*r*-DVB₃₀) films was measured by FT-IR. Variation in transmittance according to thermal treatment time and temperature.



Figure S11. DMA curves of $poly(S_{70}-r-DVB_{30})$ films thermally treated at 110 °C for a) 1 h, b) 2 h, c) 6 h, d) 12 h, e) 24 h, f) 48 h.



Figure S12. DMA curves of $poly(S_{70}-r-DVB_{30})$ films thermally treated at 140 °C for a) 1 h, b) 2 h, c) 6 h, d) 12 h, e) 24 h, f) 48 h.



Figure S13. a) DMA curves of $poly(S_{70}-r-DVB_{30})$ film without thermal treatment. DMA curves of $poly(S_{70}-r-DVB_{30})$ films thermally treated at 170 °C for b) 1 h, c) 2 h, d) 6 h.



Figure S14. Degradation temperatures (2% weight loss) of neat $poly(S_{70}-r-DVB_{30})$ and $poly(S_{70}-r-DVB_{30})$ thermally treated at 140 °C for 12, 24, and 48 h.



Figure S15. Measured T_g by maximum tan δ from DMA results. Samples treated at 170 °C for more than 12 h were crushed during the clamping and their elastic modulus could not be measured.