

Supporting Information

Understanding the enhancement and temperature-dependency of the self-healing and electromechanical properties of dielectric elastomers containing mixed pendant polar groups

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As seen in Figure S1a and S2, the characteristic alkene peak for SBS at 5.4 ppm disappeared after the reaction. In turn, a CH₃ peak at 3.7~3.8 ppm appeared for MG for the terminus of the grafted ester, whilst a CH₂ peak at 3.2 ppm was observed for MG and TG. The overall grafting efficiency for the thiol-ene reaction was 97.2%, 97.5%, 97.8% and 93.4% for 100/0, 95/5, 90/10 and 80/20 MG/TG-SBS respectively. For calculation of the ratio of MG/TG, the total grafting was derived from the reduction in the alkene peak at 5.4 ppm. This was compared to the CH₃ grafting peak at 3.7~3.8 ppm and the difference between the two was taken as the TG group grafting. Therefore, the absolute grafting ratios for 95/5, 90/10 and 80/20 MG/TG-SBS was 94.9/5.1%, 87.9/12.1% and 73.4/26.6% respectively.

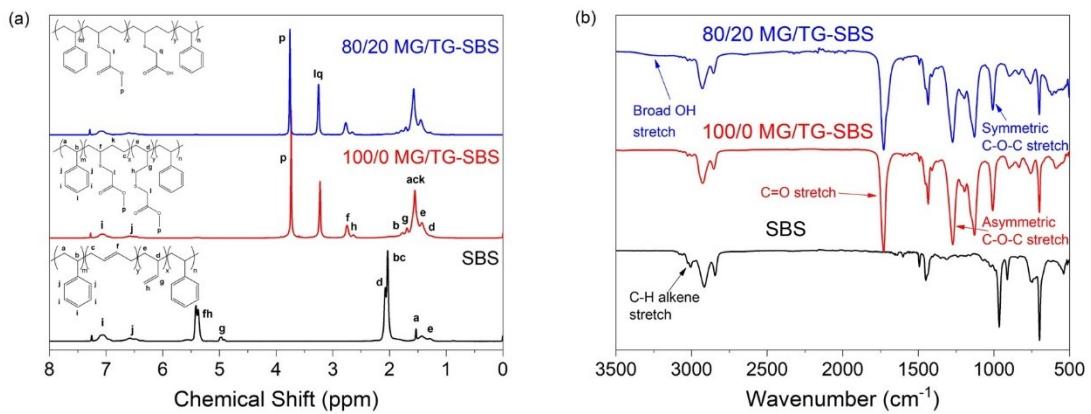


Figure S1 (a) ^1H NMR spectroscopy of SBS, 100/0 MG/TG-SBS and 80/20 MG/TG-SBS and (b) FTIR spectroscopy of SBS, 100/0 MG/TG-SBS and 80/20 MG/TG-SBS

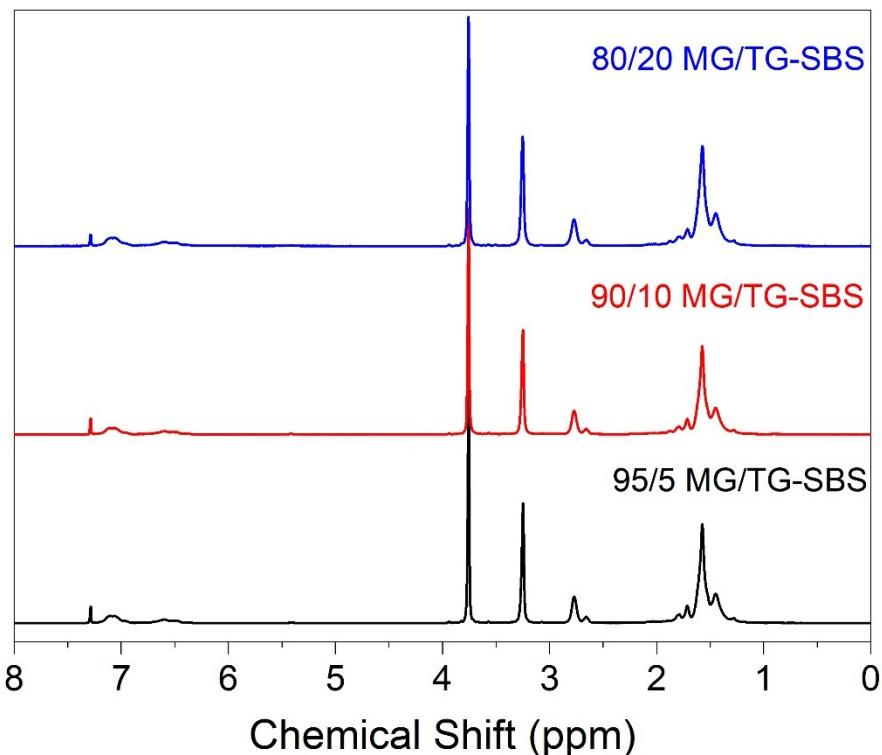


Figure S2 ^1H NMR spectroscopy of 95/5, 90/10 and 80/20 MG/TG SBS

Fourier transform infrared spectroscopy (FTIR) results in Figure S1b and S3 show that after modification, the characteristic alkene group at 3006 cm $^{-1}$ disappears, and new peaks associated with ester and carboxylic acid groups appear, where a C=O peak forms at 1730 - 1735 cm $^{-1}$, and a symmetric C-C-O stretch appears in all of the modified elastomers. In MG/TG-SBS, this appears as a stretch at 1007 cm $^{-1}$ whilst the asymmetric C-C-O stretch is observed as a stretch

for MG/TG-SBS at 1277 cm^{-1} . Finally, in MG/TG-SBS there is a broad peak between 3200 cm^{-1} and 3400 cm^{-1} attributed to the OH group of TG. This peak increases in intensity as the TG ratio increased. Overall, ^1H NMR and FTIR results confirm the successful grafting of MG and TG to SBS to form MG/TG-SBS.

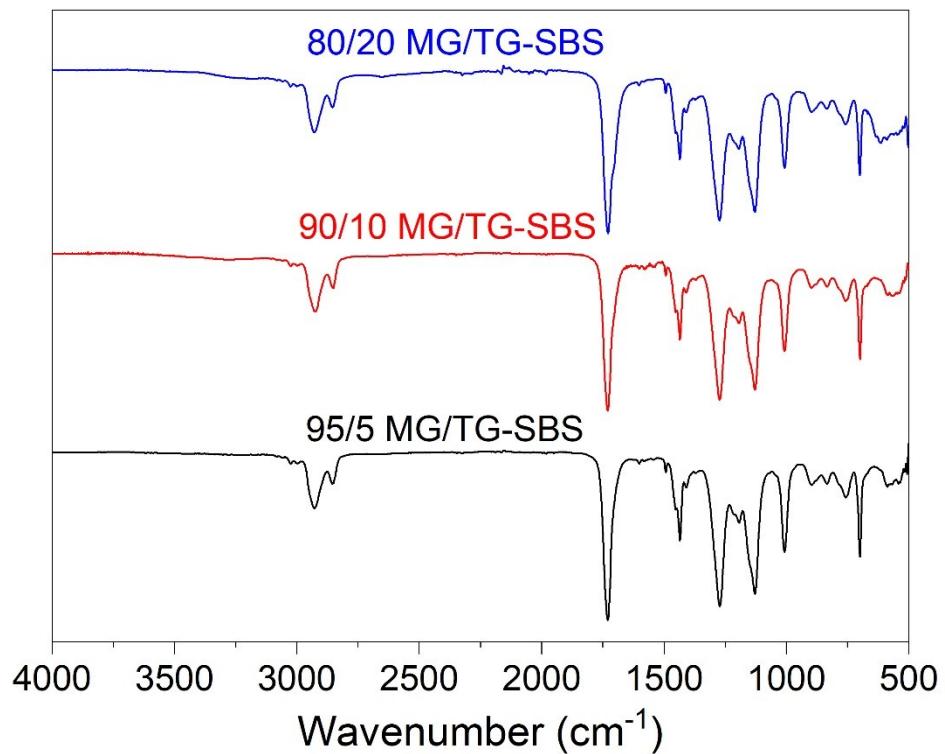


Figure S3 FTIR spectroscopy of 95/5, 90/10 and 80/20 MG/TG-SBS

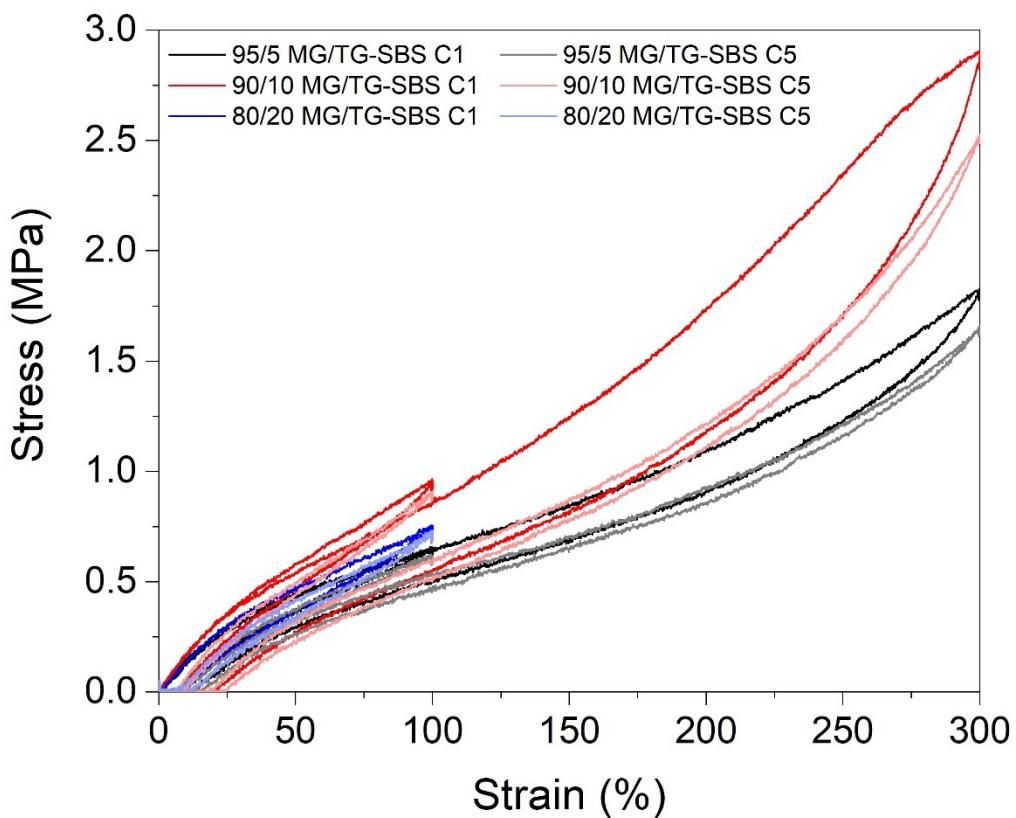


Figure S4 1st and 5th cycles of cyclic stress softening for 95/5, 90/10 and 80/20 MG/TG-SBS

3.3 Synergetic effects of MG/TG on electrical properties

From Figure S5a, unmodified SBS has a relative permittivity of $\epsilon_r \sim 2.8$ at 10^3 Hz. Modification with 100/0 MG/TG enhanced the permittivity to $\epsilon_r \sim 11.4$ at 10^3 Hz. It was expected that due to the increased polarity of a carboxylic acid group compared to an ester group, the relative permittivity would increase further with additional thioglycolic acid grafting. However, the opposite was observed whereby the permittivity dropped upon grafting. The decrease was to $\epsilon_r \sim 9.2$ at 10^3 Hz for 95/5, 90/10 and 80/20 MG/TG-SBS. Interestingly, the lower than expected improvement of the relative permittivity has also been observed in the literature before when grafting purely thioglycolic acid to SBS; this resulted in a permittivity of $\epsilon_r \sim 7.2$ at 10^3 Hz.¹⁻³ It may be possible that the decrease in permittivity is due to the formation of thioglycolic acid dimers through hydrogen bonding. The dimerization reduces the change in polarity across the polymer as it reduces the charge difference across the carboxylic acid.

In terms of dielectric loss, all elastomers exhibited a low $\tan \delta$ loss of 0.01~0.02 at 10³ Hz, where $\tan \delta$ = dielectric loss/ real permittivity, demonstrating a high potential efficiency for energy transduction as shown in Figure S5b. The highly insulating and dielectric nature of SBS is observed in the AC conductivity of $\sigma_{AC} = 1 \times 10^{-9} \text{ S m}^{-1}$ at 10³ Hz in Figure S5d. The chemically modified elastomers have a higher conductivity of one order of magnitude compared to SBS, which deviates and grows at low frequency to a large difference in conductivities. At 1 Hz, the difference in AC conductivity between SBS and MG/TG SBS is three orders of magnitude, as the AC Conductivity of SBS decreases to $1 \times 10^{-12} \text{ S m}^{-1}$ whilst MG/TG SBS remain at $\sigma_{AC} = 1 \times 10^{-9} \text{ S m}^{-1}$. All of the elastomers maintain a phase angle of 90 ° above 1 kHz in Figure S5c, indicating further their insulating nature.

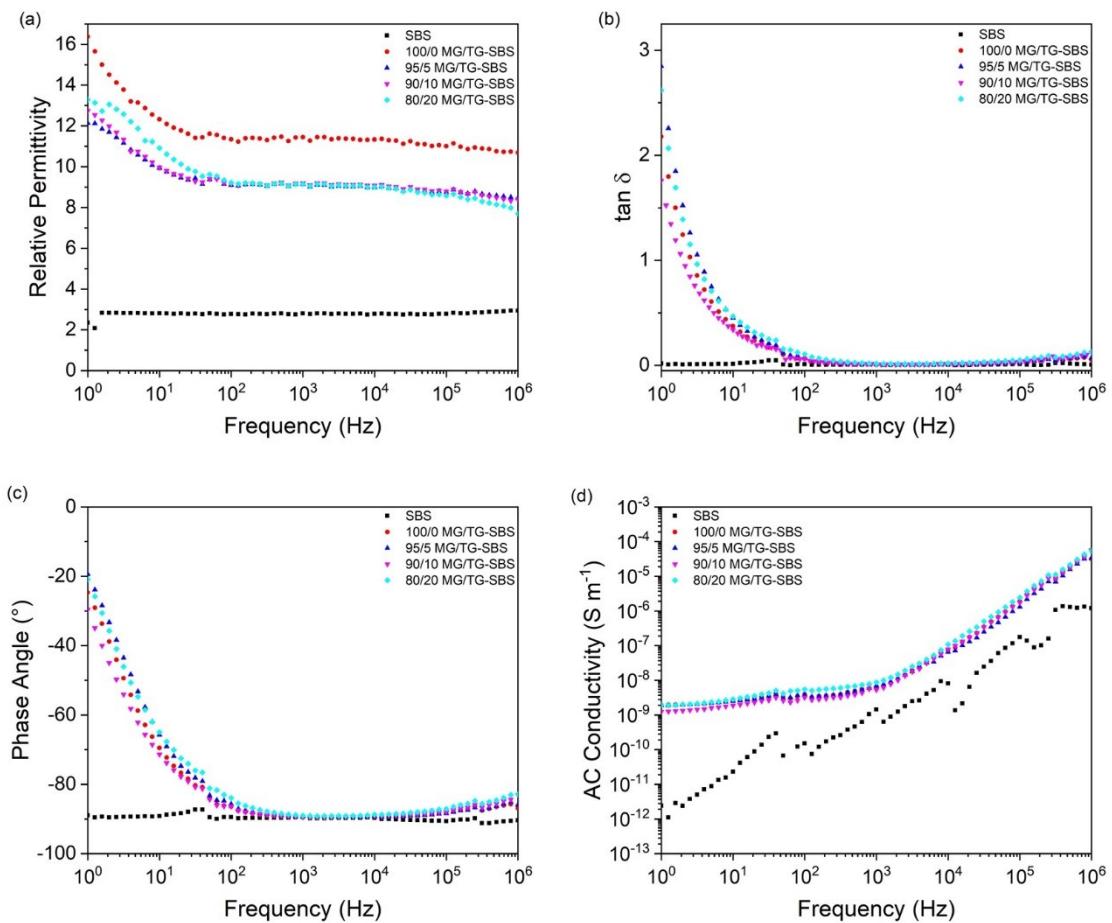


Figure S5 Impedance spectroscopy showing (a) the relative permittivity, (b) $\tan \delta$, and (c) phase angle (d) AC conductivity for SBS, 100/0, 95/5, 90/10 and 80/20 MG/TG-SBS vs frequency

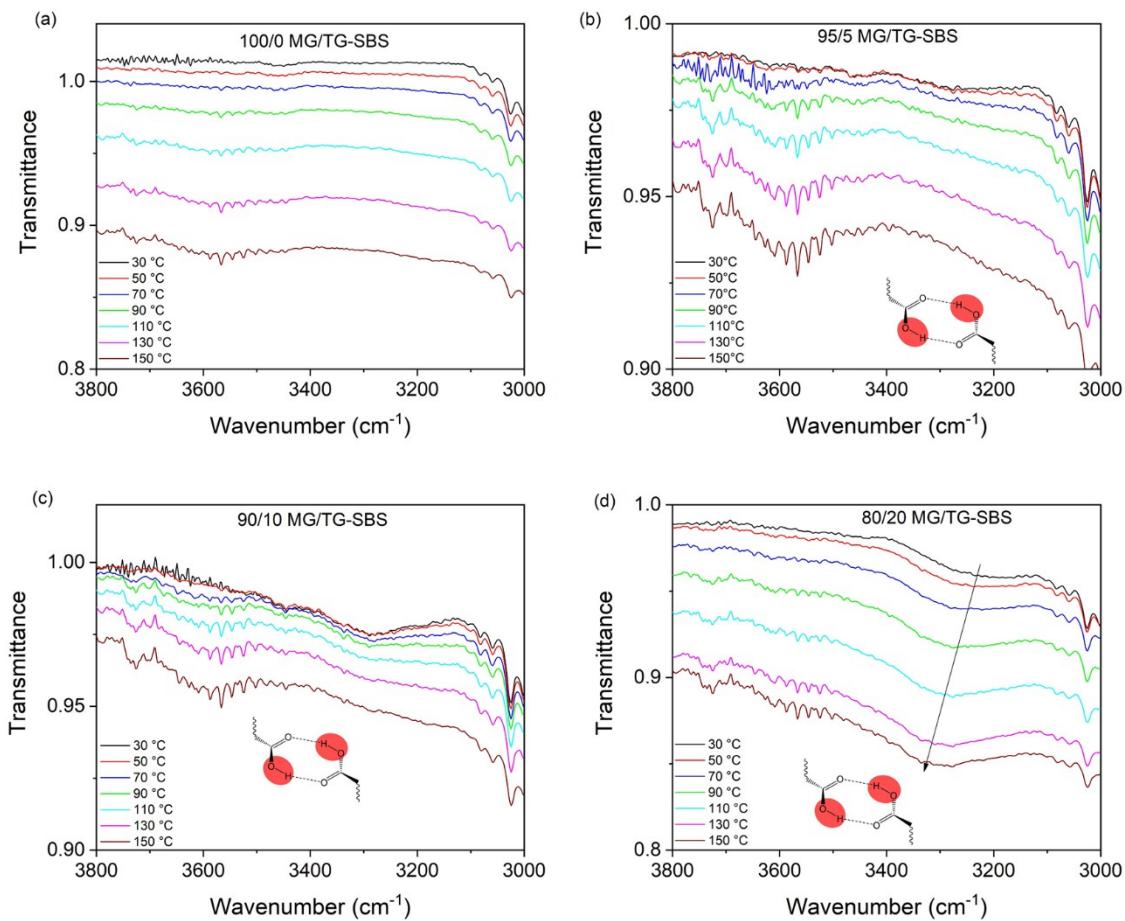


Figure S6 Temperature dependant FTIR for 100/0, 95/5, 90/10 and 80/20 MG/TG-SBS at 3320 cm^{-1} upon heating

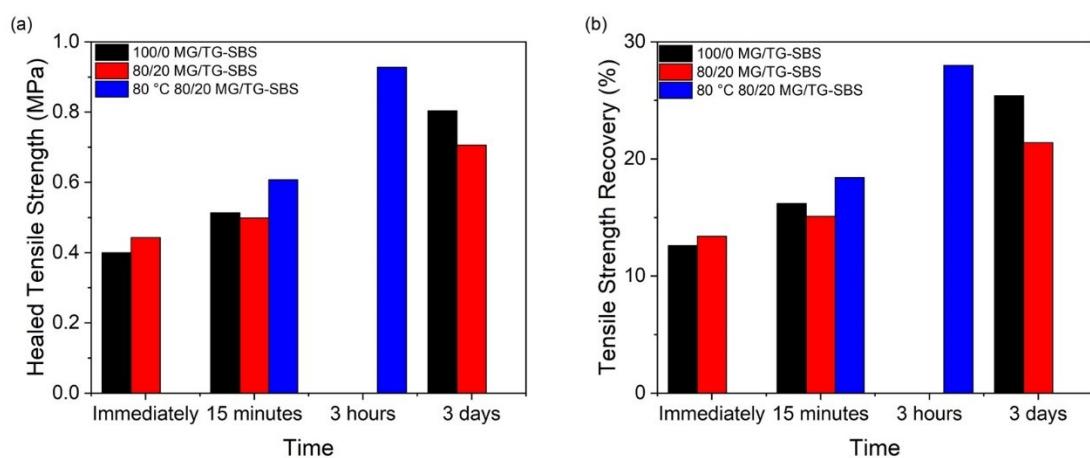


Figure S7 (a) Healed tensile strength and (b) tensile strength recovery of both room temperature and 80 °C self-healing of 100/0 and 80/20 MG/TG-SBS at different time steps

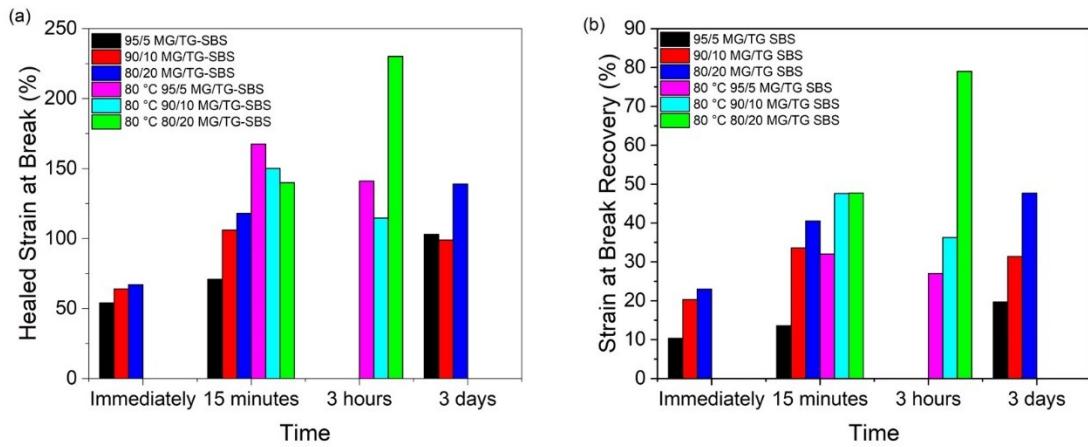


Figure S8 (a) Healed strain at break and (b) strain at break recovery for 95/5, 90/10 and 80/20 MG/TG-SBS at room temperature and at 80 °C at different time steps

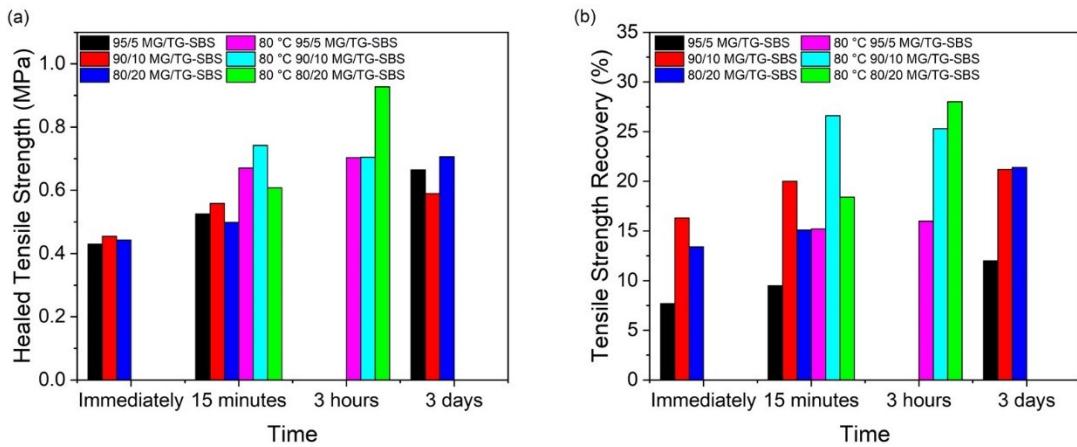


Figure S9 (a) Healed tensile strength and (b) tensile strength recovery of both room temperature and 80 °C self-healing of 95/5, 90/10 and 80/20 MG/TG-SBS at different time steps

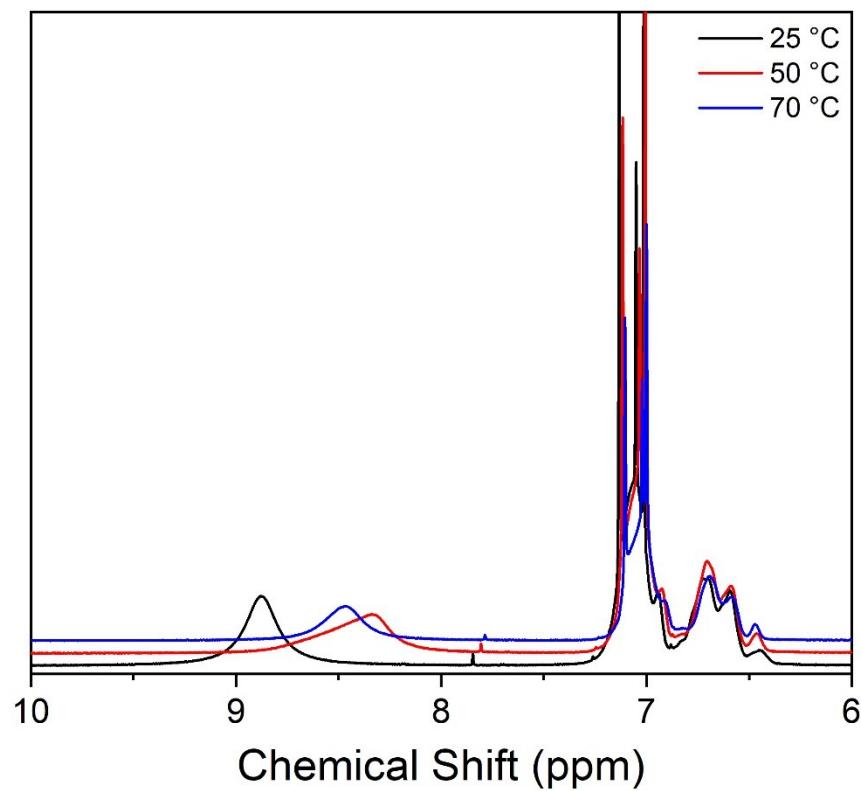


Figure S10 Variable temperature ^1H NMR of 80/20 MG/TG SBS between 6 and 10 ppm, showing the $-\text{OH}$ peak of grafted thioglycolic acid and aromatic region of styrene in SBS in toluene-d8

1. M. Tian, H. Yan, H. Sun, L. Zhang and N. Ning, *RSC Adv.*, 2016, **6**, 96190-96195.
2. C. Ellingford, C. Wan, Ł. Figiel and T. McNally, *Composites Communications*, 2018, **8**, 58-64.
3. C. Ellingford, R. Zhang, A. M. Wemyss, C. Bowen, T. McNally, Ł. Figiel and C. Wan, *ACS Appl. Mater. Interfaces*, 2018, DOI: 10.1021/acsami.8b13785.