Electronic Supplementary Information

Graphene as a prominent antioxidant for diolefin elastomers

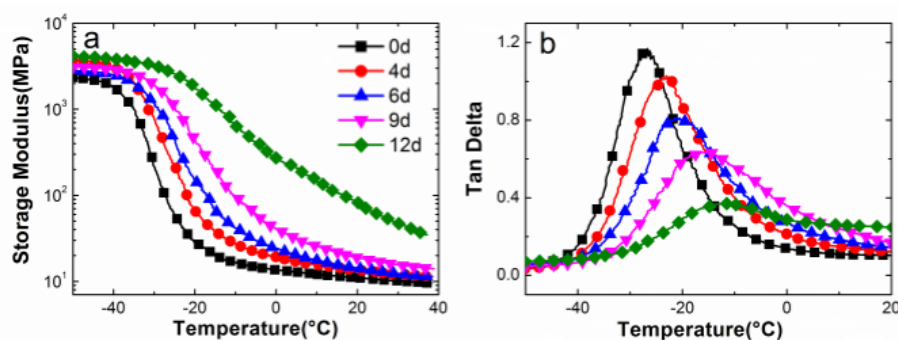Maozhu Tang,‡ Wang Xing,‡ Jinrong Wu,* Guangsu Huang,* Kewei Xiang, Lili Guo, and Guangxuan Li

Fig. S1. Dynamic mechanical properties of SBR/GE-5 aged for different days at 90º: (a) storage modulus versus temperature; (b) loss factor versus temperature.
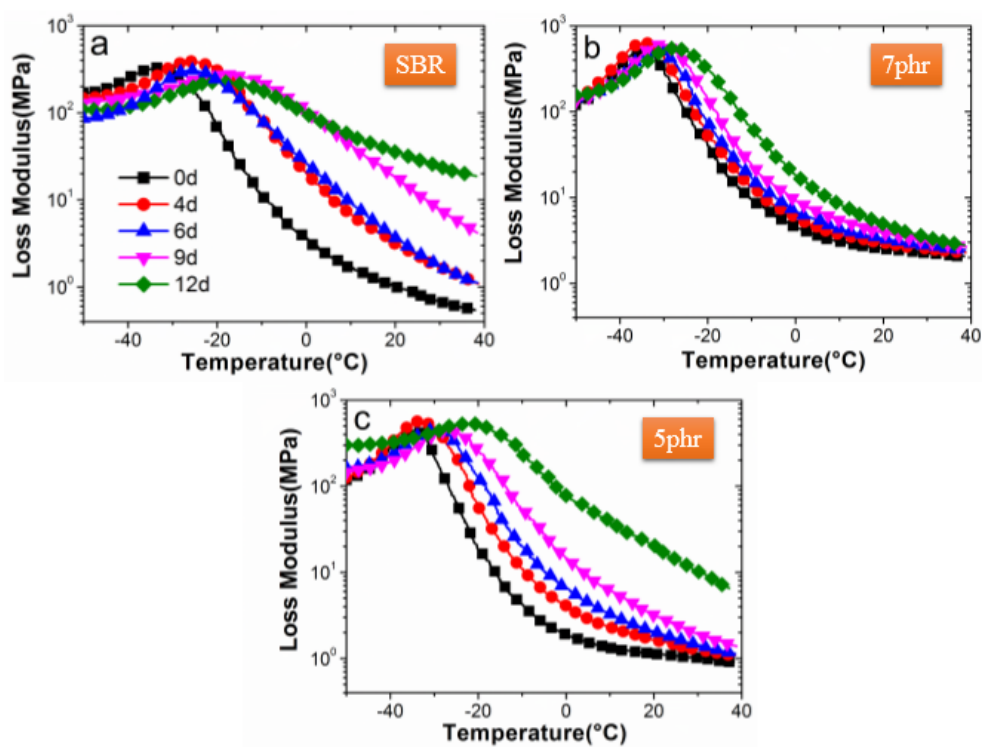

Fig. S2. The effect of thermal ageing on the loss modulus (E'') of (a) the unfilled SBR, (b) the SBR/GE-7 and (c) the SBR/GE-5.
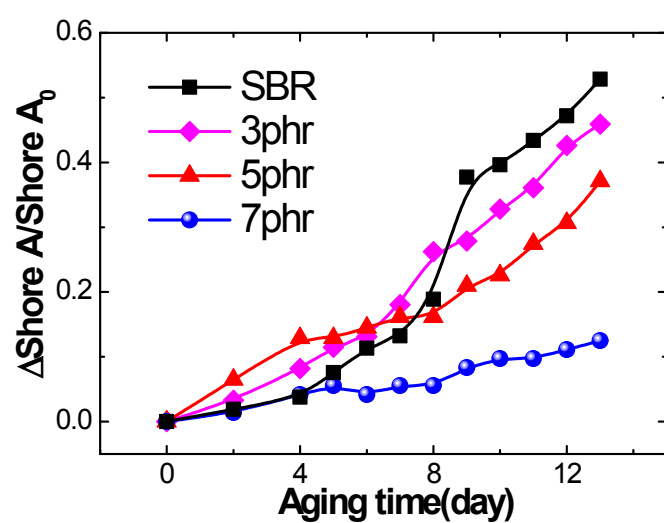
Fig. S3. The effect of aging time on the change in Shore A hardness divided by initial Shore A hardness ($\triangle$Shore A/Shore A_0) of pure SBR, GE/SBR-3, GE/SBR-5 and GE/SBR-7.
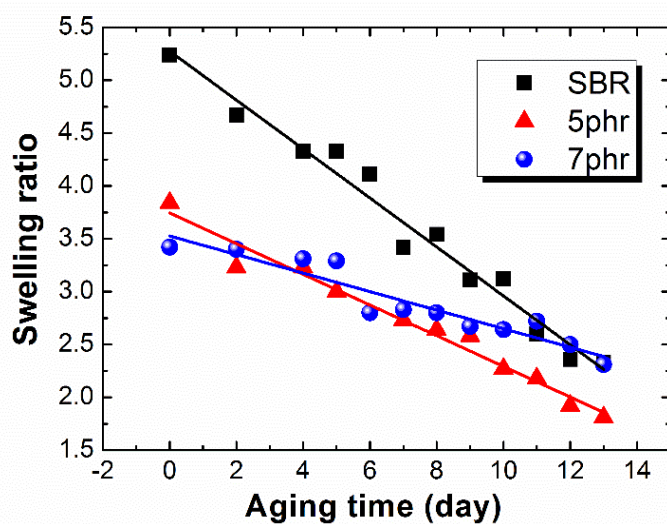

Fig. S4. Effect of ageing time on the equilibrium swelling ratio of the unfilled SBR and GE/SBR nanocomposites.
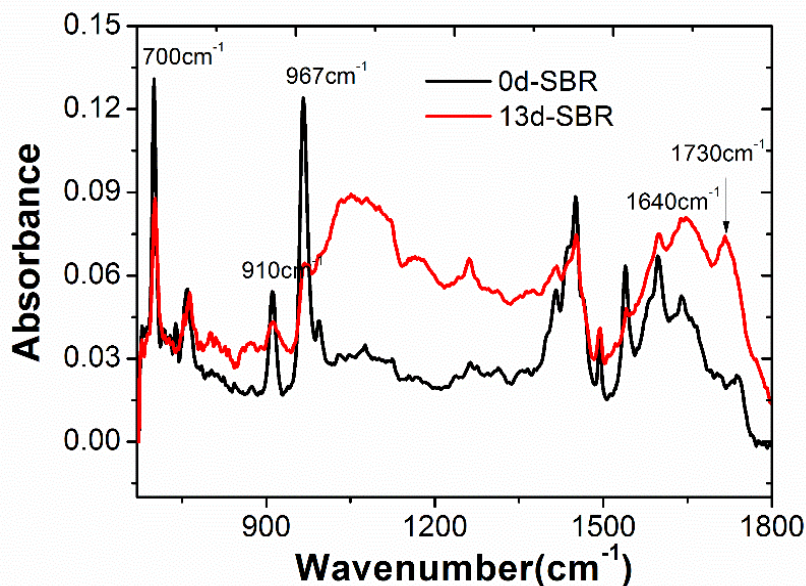
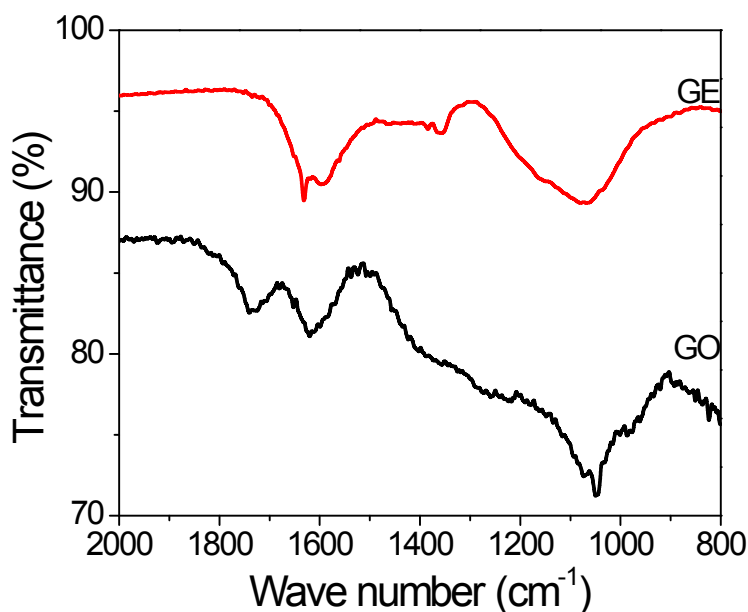Fig. S5. Representative FTIR spectra of the unfilled SBR on the external surface at different aging days.

Fig. S6. FTIR spectra of graphene oxide and chemically reduced graphene.

Analysis of the double bonds. The characteristic peak at 1640 cm^{-1} is assigned to stretching vibrations of C=C double bonds. Nevertheless, this peak significantly overlaps with other peaks of benzene rings and carbonyl species, thus it cannot be used to quantify the evolution of aliphatic double bonds. But the peaks centered at 967 cm^{-1}, 910 cm^{-1} and 700 cm^{-1} (corresponding to the C-H out of plane deformation from 1, 4-trans vinyls, 1, 2-vinyls and 1, 4-cis vinyls, respectively) are

rather independent, thus can be used to indicate the variation of aliphatic double bonds. Fig.S6 shows that the relative intensity of these three peaks decrease more rapidly for the unfilled SBR than SBR/GE-7 upon ageing. The decrease is mainly attributed to the elimination of C=C double bonds by primary macroradicals, peroxy radicals, alkoxy radicals, etc., which ultimately evolve into crosslinking points or carbonyl species.
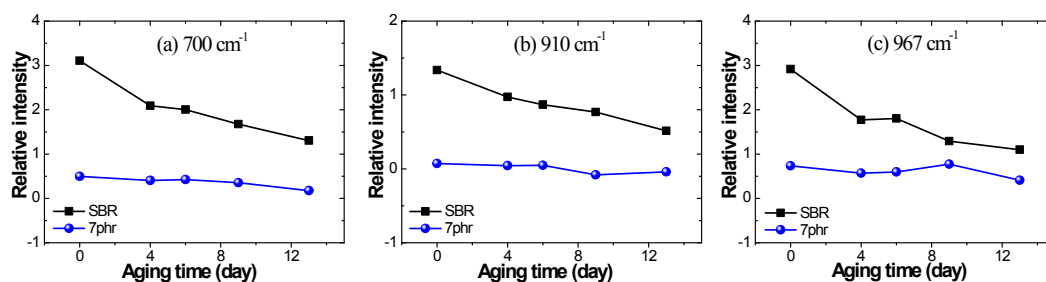

Fig. S7. Relative absorbance of (a) C-H out of plane deformation from 1, 4-cis vinyls at 700 cm^{-1} versus ageing time, (b) C-H out of plane deformation from 1, 2-vinyls at 910 cm^{-1} versus ageing time, and (c) C-H out of plane deformation from 1, 4-trans vinyls at 967 cm^{-1} versus ageing time of the unfilled SBR and SBR/GE-7.

Analysis of latex particles' sizes. The particle size distribution of SBR latex was measured by a laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd). The scanning rate is 1000 times/min.
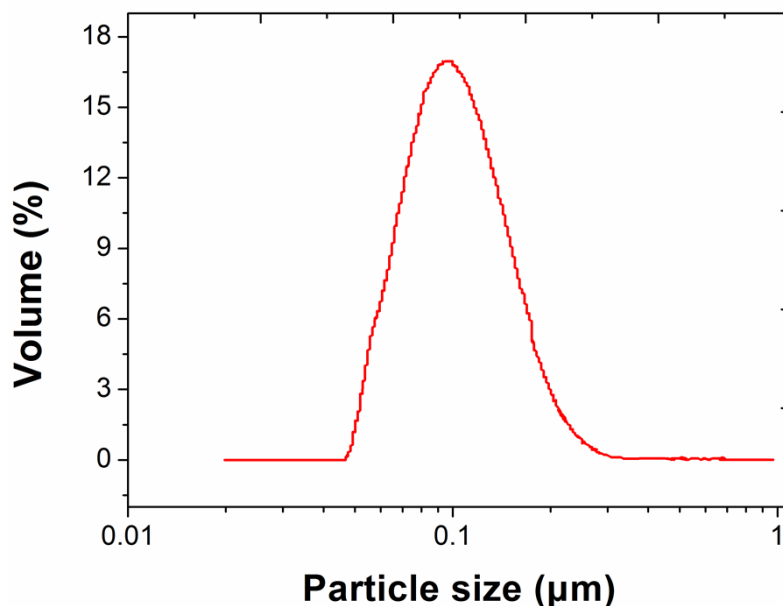

Fig. S8. Particle size distribution of SBR latex determined by a granulometer.

The calculation of crosslinking density. On the basis of the Flory–Rehner equation, the crosslinking density was determined from equilibrium swelling measurements:

$$-[Ln(1-v_r)+v_r+\chi v_r^2]=V_0 n\left(v_r^{1/3}-v_r/2\right) \tag{1}$$

where v_r is the volume fraction of the rubber in the swollen mass, V_0 is the molar volume of the solvent (106.2 cm^3 for toluene), n is the number of active network chain segments per unit of volume (crosslinking density), and χ is the Flory–Huggins polymer–solvent interaction term. The value of χ for SBR in toluene is 0.391[1].The value of v_r was attained according to:

$$v_r=\frac{w_2/\rho_2}{w_2/\rho_2+(w_1-w_2)/\rho_1} \tag{2}$$

where ρ_1 and ρ_2 are the densities of the solvent and the rubber, respectively.

References

[1]. Bristow, G.M. and W.F. Watson, Cohesive energy densities of polymers. Part 1.—Cohesive energy densities of rubbers by swelling measurements. Transactions of the Faraday Society, 1958. 54: p. 1731-1741.