Electronic Supplementary Information

Toughening rubbers with hybrid filler network of graphene and carbon nanotubes

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Raman measurements were carried out to demonstrate the successful reduction of GO. As shown in Fig. S1, the first order Raman spectrum of graphite oxide contains a G band at 1588 cm⁻¹ and a D band at 1347 cm⁻¹, corresponding to the in-phase vibration of the graphite lattice and the structural defects, respectively. After reduction, the intensity ratio of D band to G band (I_D/I_G) increases from 0.89 for graphite oxide to 1.38 for graphene. This increase is attributed to the smaller size of numerous newly-formed graphitic domains with defects¹⁻⁵. The I_D/I_G values are 1.40 and 1.37 in the GE/NR nanocomposite with 3 and 5 phr graphene, respectively. These values are basically equal to that of graphene prepared by chemical reduction in aqueous suspension, suggesting that graphene oxide is effectively reduced in the nanocomposites.



Fig. S1. Raman spectra of graphite oxide, graphene and NR/GE nanocomposites with 3 and 5 phr graphene.

To further demonstrate the hybrid filler network and the sacrificial bonds, we investigate the rheological behavior of pure GO and hybrid GO/CNTs aqueous suspensions (we cannot measure the CNTs suspension because CNTs cannot form stable suspension). Using aqueous suspensions allows us to directly probe the filler network, while excluding other effects in the rubber nanocomposites such as rubber crosslink, molecular entanglement and rubber-filler interaction. The rheological measurements show that the storage modulus (G') has a plateau at low frequencies and is higher than the loss modulus (G") for both pure GO and GO/CNTs suspensions, as shown in Fig. S2a; this observation suggests the suspensions are pseudo-solid like due to the formation of instantaneous filler network in the suspensions. Moreover, G' and G" of the hybrid GO/CNTs suspension are more than one order of magnitude higher than those of pure GO suspension at the same filler concentration; this suggests that the filler network is more compact in the hybrid GO/CNTs suspension. Shearing at a high strain easily breaks the filler network, as demonstrated by the dramatic decrease of G' and G" in Fig. S2b. Moreover, the rupture of the filler network leads to a liquid-like behavior of the suspensions, thus G' becomes lower than G''. The easiness of rupture of the filler network can be attributed to the weak π - π interaction between GO and CNTs that has a bond energy between 20k_BT and 40k_BT. ^{6, 7} The rupture of the filler network provides sacrificial bonds that dissipate energy, which serves as the toughening mechanism for the rubber nanocomposites of this work. The filler network can be partially restored immediately after the high-strain shearing, as shown by the recovery of G' and G" in Fig. S2b&c. Thus, under dynamic loadings, the NR/GE/CNTs nanocomposites still show higher energy dissipation than other nanocomposites filled with single-component fillers. This is probably the reason for the slower crack-growth rate of the NR/GE/CNTs nanocomposites.'



Fig. S2. Rheological behaviors of pure GO and hybrid GO/CNTs suspensions. These suspensions have a total nanofiller weight fraction of 1 wt%. The weight ratio of GO to CNTs is 1:1 in the hybrid GO/CNTs suspension. (a) Frequency dependence of G' and G''; (b) effect of high strain shear on the rheological property of the hybrid GO/CNTs suspension, here the

strain is 300% and the frequency is 1 Hz; (c) frequency dependence of G' and G" before and after high strain shear. The filled and open symbols correspond to G' and G", respectively.

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