SUPPORTING INFORMATION

DESIGN OF RUBBER COMPOSITES WITH AUTONOMOUS SELF-HEALING CAPABILITY

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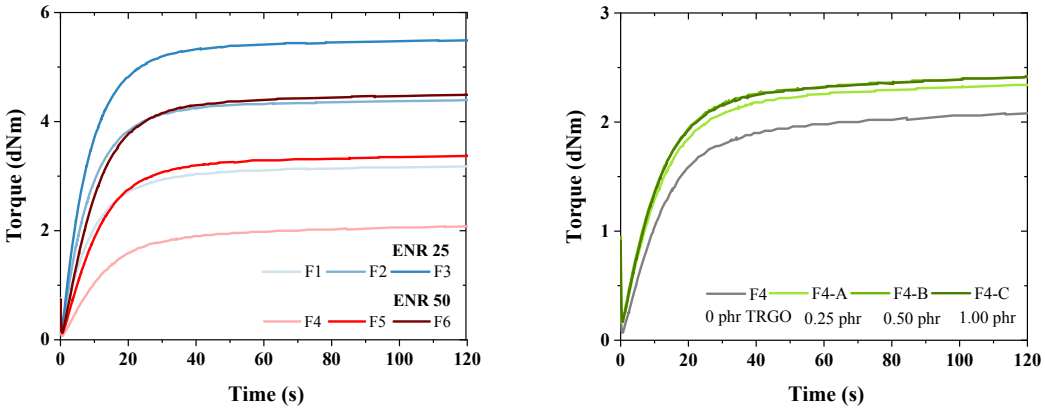
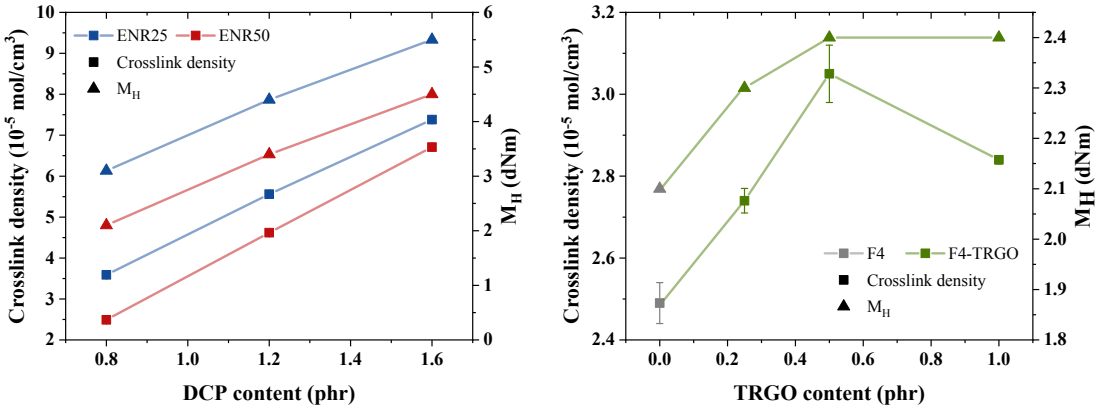
SI.1. Curing curves and crosslink density of ENR compounds and ENR-TRGO nanocomposites



a) b)

Figure S 1. a) Curing curves of ENR compounds, b) Curing curves of ENR-TRGO nanocomposites.



a) b)

Figure S 2. a) Crosslink density of ENR compounds, b) Crosslink density of ENR-TRGO nanocomposites.

SI.2. Mechanical properties of ENR compounds.

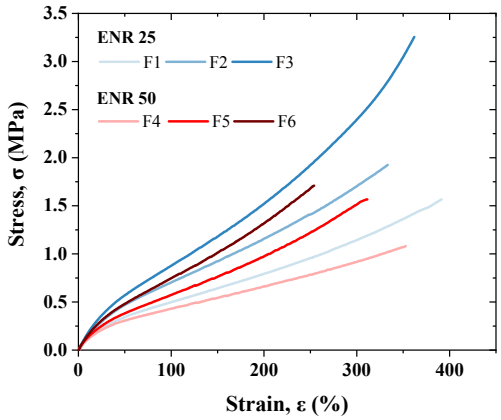


Figure S 3. Stress-strain curves of ENR compounds.

Table S 1. Mechanical properties of ENR compounds.

Compound	M_H (dN.m)	$\nu \cdot 10^{-5}$ (mol/cm^3)	M_{100} (MPa)	M_{300} (MPa)	σ_R (MPa)	ε_R (%)
F1	3.14 ± 0.04	3.59 ± 0.05	0.51 ± 0.01	1.16 ± 0.01	1.58 ± 0.02	394 ± 04
F2	4.36 ± 0.04	5.57 ± 0.03	0.70 ± 0.01	1.70 ± 0.01	1.90 ± 0.04	328 ± 06
F3	5.48 ± 0.01	7.38 ± 0.09	0.87 ± 0.01	2.44 ± 0.05	3.2 ± 0.1	350 ± 12
F4	2.08 ± 0.01	2.49 ± 0.05	0.45 ± 0.02	0.95 ± 0.03	1.08 ± 0.03	349 ± 18
F5	3.38 ± 0.01	4.63 ± 0.02	0.59 ± 0.02	1.52 ± 0.01	1.61 ± 0.05	315 ± 08
F6	4.50 ± 0.00	6.71 ± 0.09	0.76 ± 0.01	2.11 ± 0.01	1.7 ± 0.3	251 ± 35

SI.3. Infrared spectra of ENR compounds.

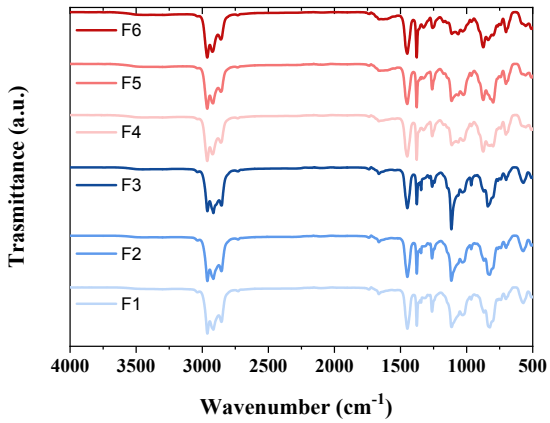


Figure S 4. Infrared spectra of ENR compounds.

SI.4. Mechanical properties of ENR-TRGO nanocomposites

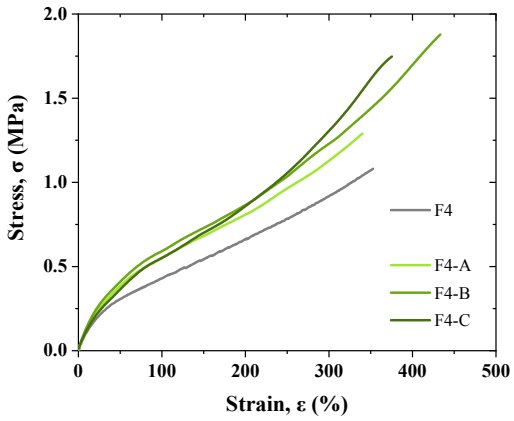


Figure S 5. Stress-strain curves of ENR-TRGO nanocomposites.

Table S 2. Mechanical properties of ENR-TRGO nanocomposites.

Compound	$\mathbf{M_H}$ (dN.m)	$\boldsymbol{\nu \cdot 10^{-5}}$ (mol/cm^3)	$\mathbf{M_{100}}$ (MPa)	$\mathbf{M_{300}}$ (MPa)	$\boldsymbol{\sigma_R}$ (MPa)	$\boldsymbol{\varepsilon_R}$ (%)
F4	2.08 ± 0.01	2.49 ± 0.05	0.45 ± 0.02	0.95 ± 0.03	1.08 ± 0.03	349 ± 18
F4-A	2.32 ± 0.03	2.74 ± 0.03	0.54 ± 0.04	0.94 ± 0.09	1.3 ± 0.2	336 ± 49
F4-B	2.42 ± 0.01	3.05 ± 0.09	0.57 ± 0.01	1.21 ± 0.02	1.85 ± 0.07	431 ± 16
F4-C	2.40 ± 0.02	2.84 ± 0.01	0.56 ± 0.01	1.29 ± 0.02	1.7 ± 0.2	376 ± 33

SI.5. Stress-strain curves of F4-B before and after healing protocol

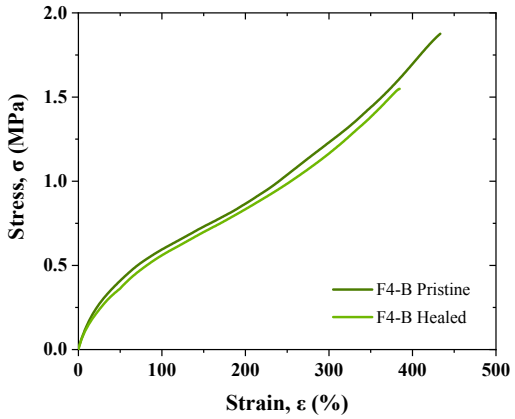


Figure S 6. Stress-strain curves of F4-B before and after healing protocol.

SI.6. Characterization of TRGO

Raman spectroscopy was carried out in a *Renishaw Invia* Raman Confocal microscope using an argon laser radiation source with an excitation wavelength of 514.5 nm. Three spectra were recorded from 250 cm^{-1} to 3000 cm^{-1}. The crystallinity and the disorder in the basal-plane were determined from the area of the peaks of the corresponding bands. FT-IR spectroscopy was used to analyze the TRGO functionalization using potassium bromide (KBr) pellets in a *Perkin Elmer* spectrometer, model UATR Two. Spectra were taken from 400 cm^{-1} to 4000 cm^{-1} with a resolution of 4 cm^{-1}. Pure KBr spectrum was used as background. X-ray photoemission spectroscopy (XPS) analysis was performed on a *Fisons MT500* spectrometer, operated at 300 W, with a non-monochromatized radiation source of MgKα of photon energy equal to 1253.36 eV. The deconvolution was done in *Origin Pro*, with a Shirley type baseline and Gaussian adjustment.

Raman spectroscopy is commonly used to analyze the graphitic quality of carbon materials by comparing the intensity ratio between the D, at 1360 cm^{-1}, and G, at 1580 cm^{-1}, bands (I_D/I_G) (Figure S7). The results reflect the structural changes occurred during the oxidation and exfoliation treatment and show a significant increase in disorder, which is usually attributed to direct damage and functionalization of the surface.

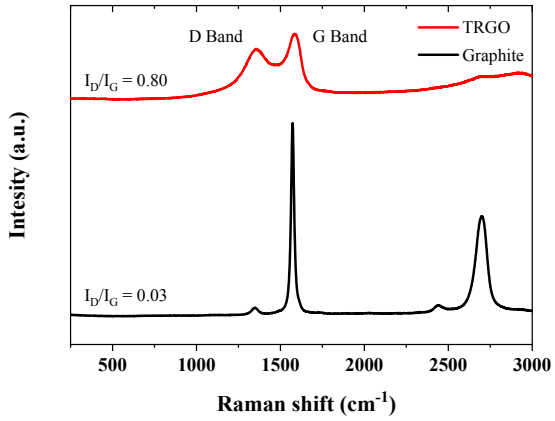


Figure S 7. Raman spectra of graphite and TRGO.

The nature of the functionalization was later established by XPS and FT-IR. The general XPS spectrum (Figure S9) reports the presence of carbon (~75 %) and oxygen (~25 %) atoms, by the relationship between their peaks and the deconvolution of the incorporated functionalities.

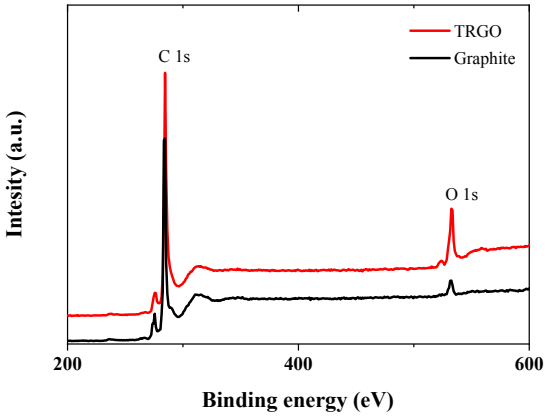


Figure S 8. General XPS spectra of graphite and TRGO.

Figure S3 shows the deconvolution performed on the C 1s and O 1s signals. Figure S9.a presents the deconvolution of the C 1s signal with the percentages of the different species. The components indicate the presence of: non-oxygenated ring C=C (sp^2 hybridization) at 284.5 eV, the C-C (sp^3 hybridization) at 285.8 eV, C-OH bonds at 286.6 eV, C-O-C group at 287.6 eV, carboxylate carbon at 288.8 eV and the π- π* interactions associated to the non-oxygenated ring C=C (sp^2 hybridization) at 291.0 eV, which reveals the success of reduction. The deconvolution performed on the signal of O 1s (Figure S9.b) is consistent with the C 1s data and reveals the presence of C-O bonds (C-OH and C-O-C) at 533.3 eV and the O associated to the carboxylate group at 531.0 eV.[1-2]

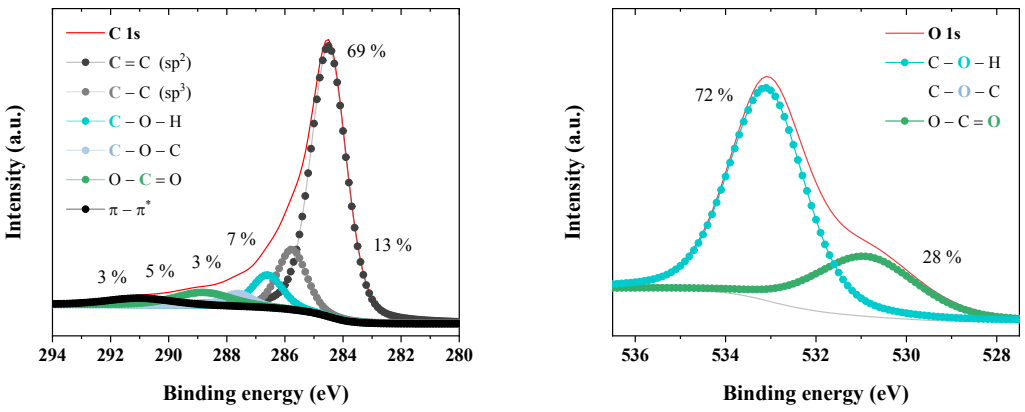
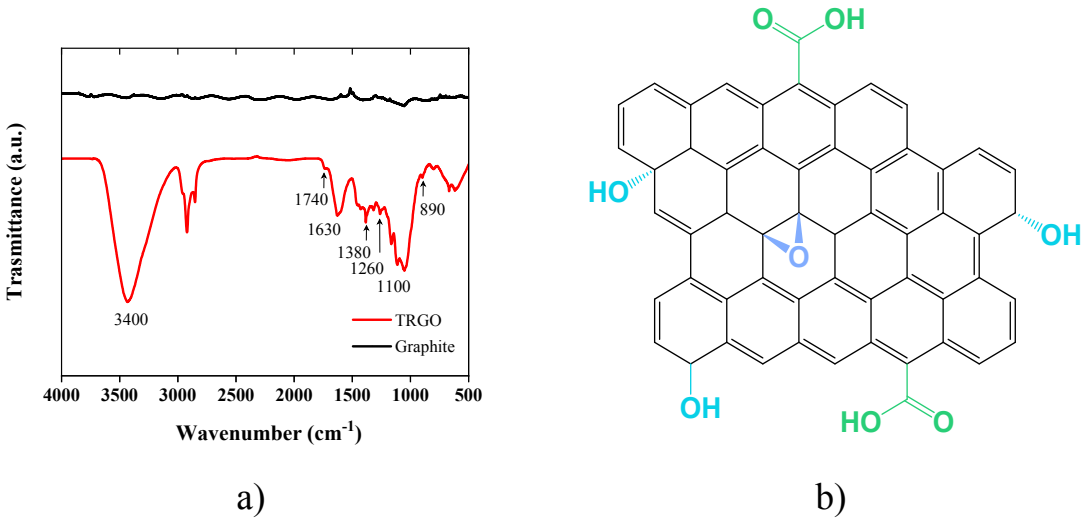


Figure S 9. Peak deconvolution of the a) C 1s and b) O 1s for TRGO.

The functional groups were corroborated by the analysis of their infrared spectrum (Figure S10). Characteristic bands of TRGO were identified at 3400 cm^{-1} (─ OH stretching vibration), at 2960 cm^{-1}, 2920 cm^{-1} and 2860 cm^{-1} (−CH stretching vibrations) and at 1630 cm^{-1} (C = C bending in cyclic bonds). As for the epoxy groups attached to the TRGO cyclic structure, its characteristic peak is identified at 890 cm^{-1}. A band at 1110 cm^{-1} is also observed for the symmetrical stretching of type C ─ O - C. A small peak is present at 1740 cm^{-1} associated with carboxylic groups, coinciding with XPS data.[3]



a) b)

Figure S 10. a) FT-IR spectrum of graphite; b) scheme of TRGO with its functional group.

REFERENCES

1. Stankovich, S.; Piner, R. D.; Chen, X.; Wu, N.; Nguyen, S. T.; Ruoff, R. S., Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly (sodium 4-styrenesulfonate). *J. Mater. Chem.* **2006,** *16* (2), 155-158.
2. Botas, C.; Álvarez, P.; Blanco, P.; Granda, M.; Blanco, C.; Santamaría, R.; Romasanta, L. J.; Verdejo, R.; López-Manchado, M. A.; Menéndez, R., Graphene materials with different structures prepared from the same graphite by the Hummers and Brodie methods. *Carbon* **2013,** *65*, 156-164.
3. Socrates, G., *Infrared and Raman Characteristic Group Frequencies*. 3rd ed.; John Wiley & Sons, LTD: England, 2001; pp 1-347.