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Supplementary information for

Localizing the cross-links distribution in elastomeric composites by tailoring the morphology of the curing activator

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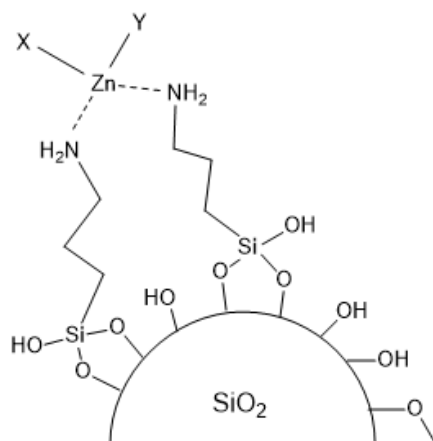


Figure S1: Proposed structure of the curing activator Zn@SiO₂, in which each Zn(II) center is coordinated by two amino groups of two APTES molecules. The other two coordination sites are supposed to be occupied by hydroxyl or nitrate groups, residual from the reaction. Reproduced from [1].

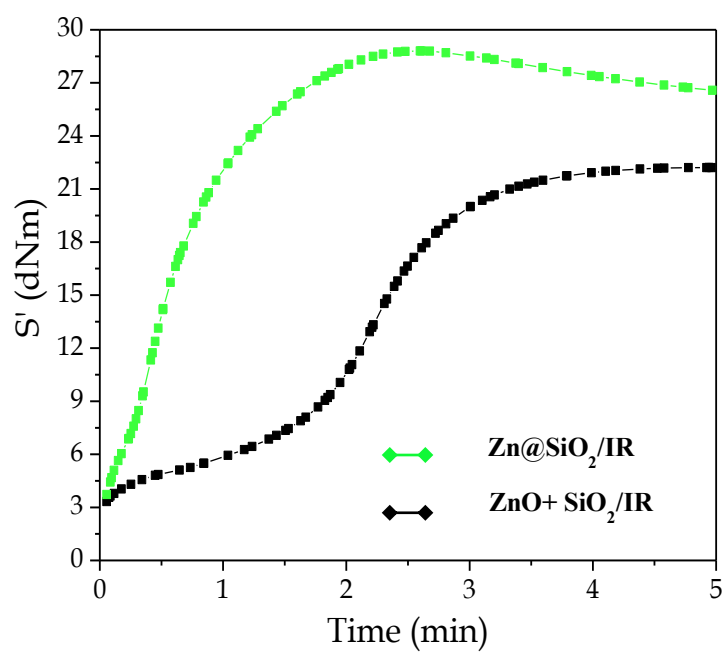


Figure S2: Vulcanization curves for Zn@SiO₂/IR (green curve) and ZnO+SiO₂/IR (black curve). Reproduced from [1].

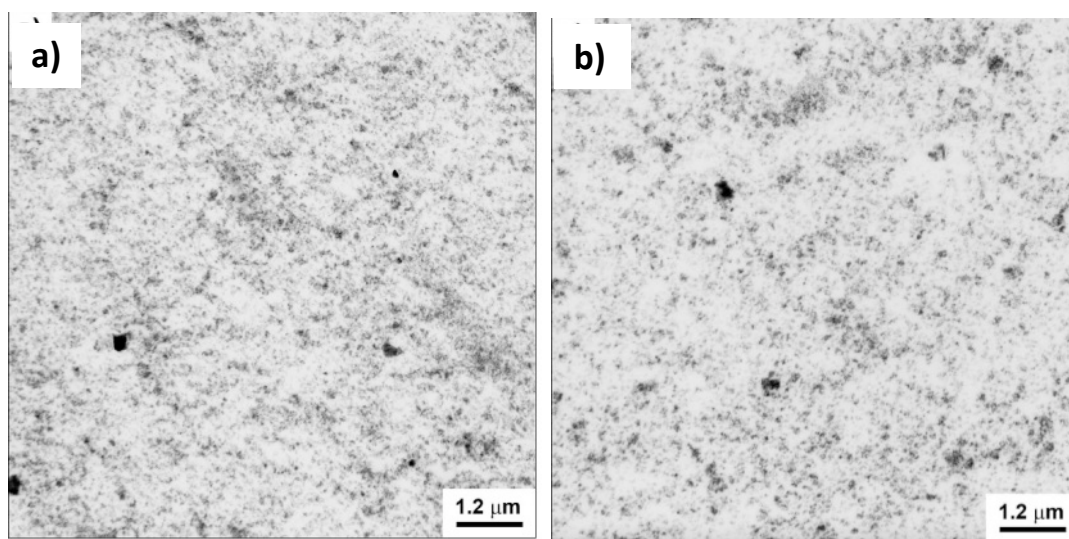


Figure S3: TEM images of vulcanized ZnO+SiO₂/IR (a) and Zn@SiO₂/IR (b) after swelling with PS.

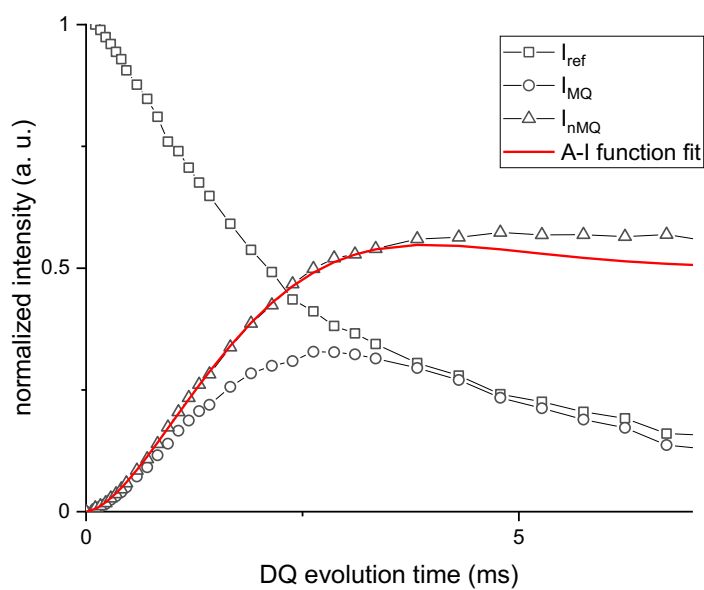


Figure S4: Reference (squares) and MQ (circles) intensities measured on ZnO+SiO₂/IR; the resulting normalized intensity is shown with triangles, and the relevant fitting with Abragam-like functions is shown with a solid red line

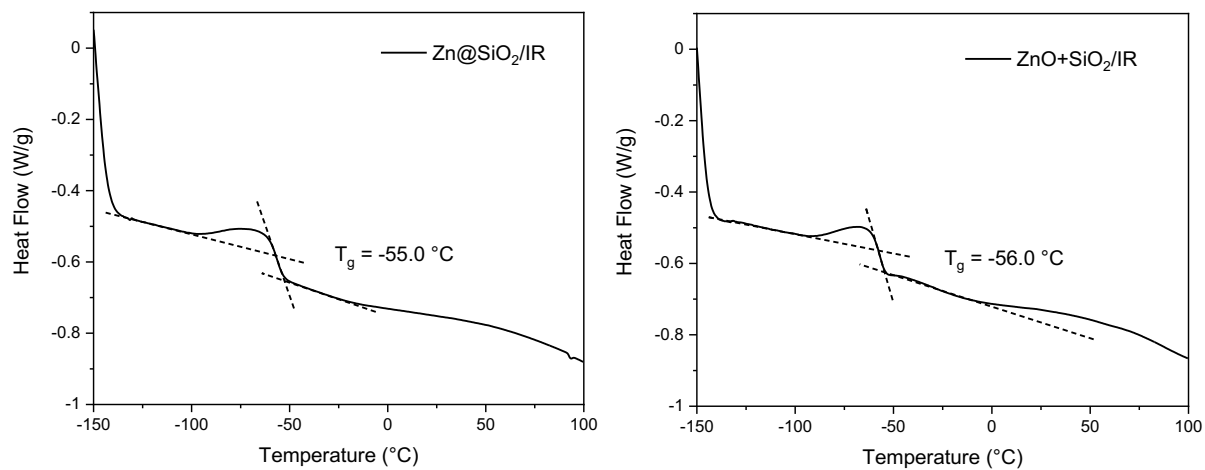


Figure S5: DSC curves of Zn@SiO₂/IR (left) and ZnO+SiO₂/IR (right) in the temperature range -150 °C – 100 °C.

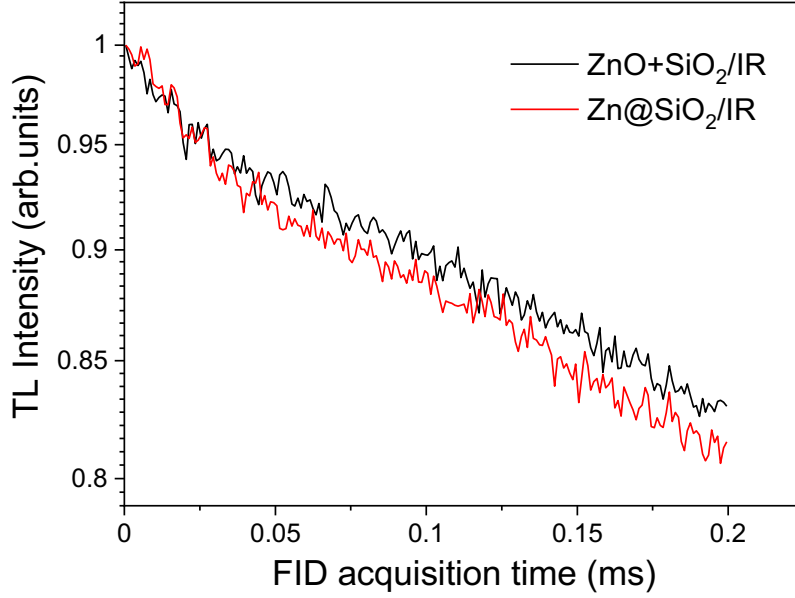


Figure S6: FID decay measured during MSE-NMR analysis.

Swelling

First, swelling experiments in toluene were performed to determine the cross-linking densities ν_{sw} of Zn@SiO₂/IR and ZnO+SiO₂/IR NCs. In a typical experiment, by measuring the mass of the swollen sample (m_{sw}) and the mass of the dried sample (m_D , after 24 hours at RT), the volumetric fraction of the swelled rubber V_R is calculated as follows:

$$V_R = \frac{(m_D - f m_0) \cdot \rho_p^{-1}}{(m_D - f m_0) \cdot \rho_p^{-1} + m_{so} \cdot \rho_s^{-1}} \quad (\text{Eq. S1})$$

where m_0 is the initial mass of the sample, m_{so} is the weight of the solvent in the swollen mass ($m_{so} = m_{sw} - m_D$), $\rho_p = 0.94 \text{ g} \cdot \text{cm}^{-3}$ is the IR density, $\rho_s = 0.87 \text{ g} \cdot \text{cm}^{-3}$ is the toluene density and f is the fraction of filler NCs as determined by TGA (% wt).

From V_R , ν_{sw} is calculated according to the Flory-Rehner equation:

$$\nu = \frac{[\ln(1 - V_R) + V_R + \chi \cdot V_R^2]}{-2 \cdot \rho_p \cdot V_s \cdot (V_R)^{1/3}} \quad (\text{Eq. S2})$$

where $V_s = 105.91 \text{ cm}^3 \text{ mol}^{-1}$ is the molar volume of toluene, χ is the Flory solvent-polymer interaction term [2], which is 0.43 for toluene-IR [3], $\rho_p = 0.94 \text{ g}\cdot\text{cm}^{-3}$ is the IR density and V_R is calculated from the experimental data as described before.

NMR

In fact, the average molecular weight between constrains (M_C) could be calculated with the following equation:

$$M_C = \frac{A}{D_{\text{res}}/2\pi} \quad (\text{Eq. S3})$$

where A is a constant dependent on the polymer repeating unit, equal to $617,000 \text{ Hz}\cdot\text{g}\cdot\text{mol}$ for IR networks. The average molecular weight M_C was related to the cross-linking density ν_{NMR} , (assuming tetra-functional cross-links) by the expression:

$$\nu_{\text{NMR}} = \frac{1}{2M_C} \quad (\text{Eq. S4})$$

Uniaxial tensile tests

From the output data, the trend of the nominal stress σ_n at increasing nominal strain ε_n was calculated according to the following equation:

$$\sigma_n = \frac{F}{A_0} \quad (\text{Eq. S5})$$

where F is the applied load, A_0 is the cross section of the undeformed specimen and ε_n was obtained as $(l-l_0)/l_0$, where l_0 and l are the initial and actual extensometer gauge length respectively. Besides, the values of load and specimen elongation were also worked out to derive the reduced stress σ^* :

$$\sigma^* = \sigma_n / \left(\lambda - \frac{1}{\lambda^2} \right) \quad (\text{Eq. S6})$$

where λ is the ratio between l and l_0 , defined as draw ratio.

The Mooney Rivlin plots are obtained by plotting the reduced stress σ^* versus the inverse $1/\lambda$ (Figure 6), which is related to the nominal strain as $\varepsilon_n = \ln\lambda$.

Fracture tests

J_c was determined following Kim and Joe [4]:

$$J_c = \eta \frac{U_c}{B(W-a_0)} \quad (\text{Eq. S7})$$

where U_c is the area under the force-displacement curve up to the fracture onset, B and W are the specimen thickness and width, a_0 is the initial crack length and η is a shape factor that changes with respect to the geometry and for pure shear configuration it is equal to 1.

References

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