Realising biaxial reinforcement via orientation-induced anisotropic swelling in graphene-based elastomers

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S1. The formation of the in-plane orientation of the filler

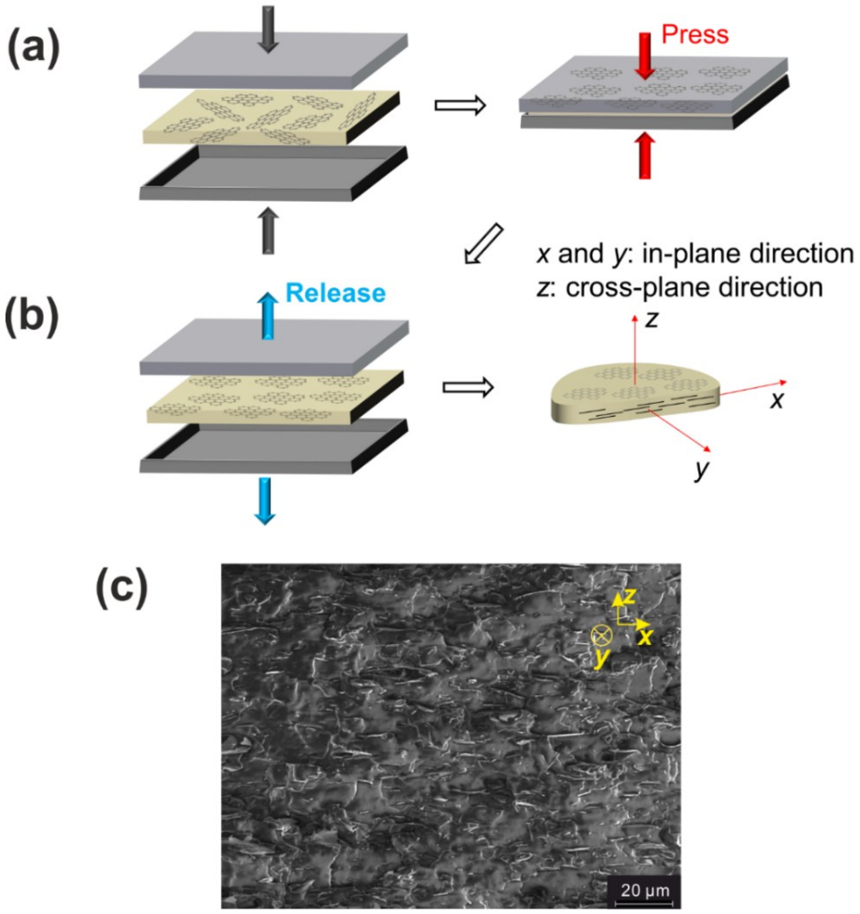

Figure S1. (a) Schematic diagram of the formation of in-plane oriented GNPs from randomly oriented GNPs in the nanocomposites under compression in the hot press; (b) Schematic diagram of the in-plane orientation of the GNP flakes in a moulded composite sheet, where *x*, *y* and *z* axes are defined; (c) SEM image of cryo-fractured cross-section of the composite sheet showing in-plane orientation with *x*, *y* and *z* axes based on (b).

S2. Mass diffusion

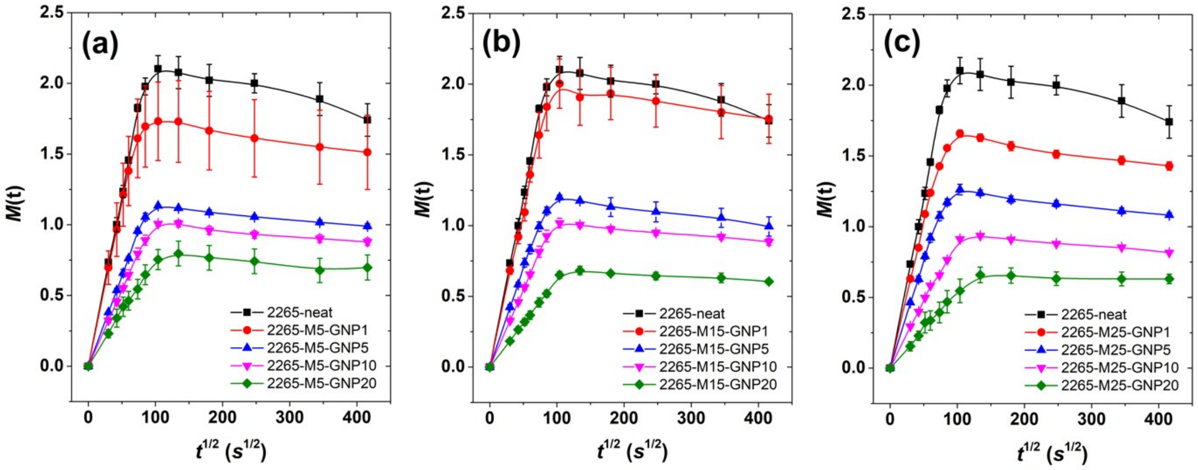

Figure S2. (a-c) The mass uptake against the root of time for the samples of M5, M15 and M25 reinforced elastomers, respectively.

S3. Dynamic mechanical analysis

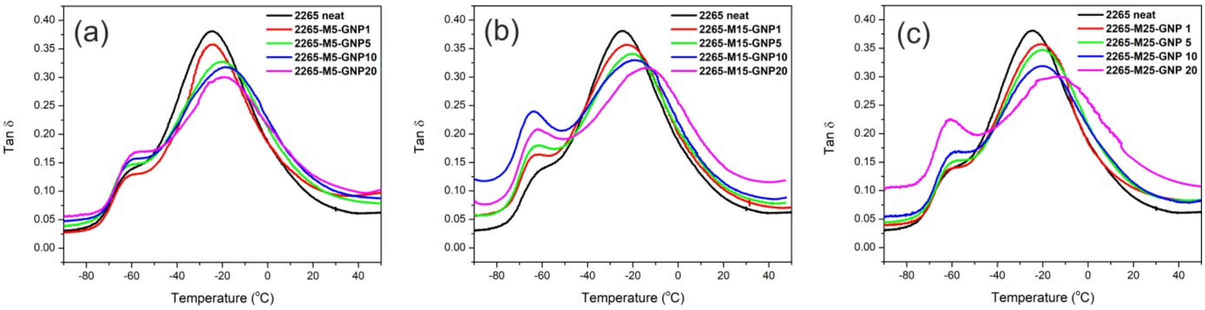

Figure S3. (a-c) The loss factor (tan *δ*) determined using dynamic mechanical analysis (DMA) of M5, M15 and M25 GNP reinforced elastomers from -90 °C to 50 °C, showing the glass transition temperature (temperature at the major peak) of the materials increases with increasing filler content.

Table S1. Glass transition temperature values determined by DMA for all the materials including neat elastomer and nanocomposites with filler loadings of 1, 5, 10 and 20 weight percent.

GNP loading (wt%)	T_g (°C) M5	T_g (°C) M15	T_g (°C) M25
0	-24.5	-24.5	-24.5
1	-24.1	-22.7	-21.0
5	-20.5	-20.3	-19.9
10	-18.8	-18.8	-19.9
20	-18.9	-13.9	-12.7

S4. Time dependence of the swelling of the materials in the solvent

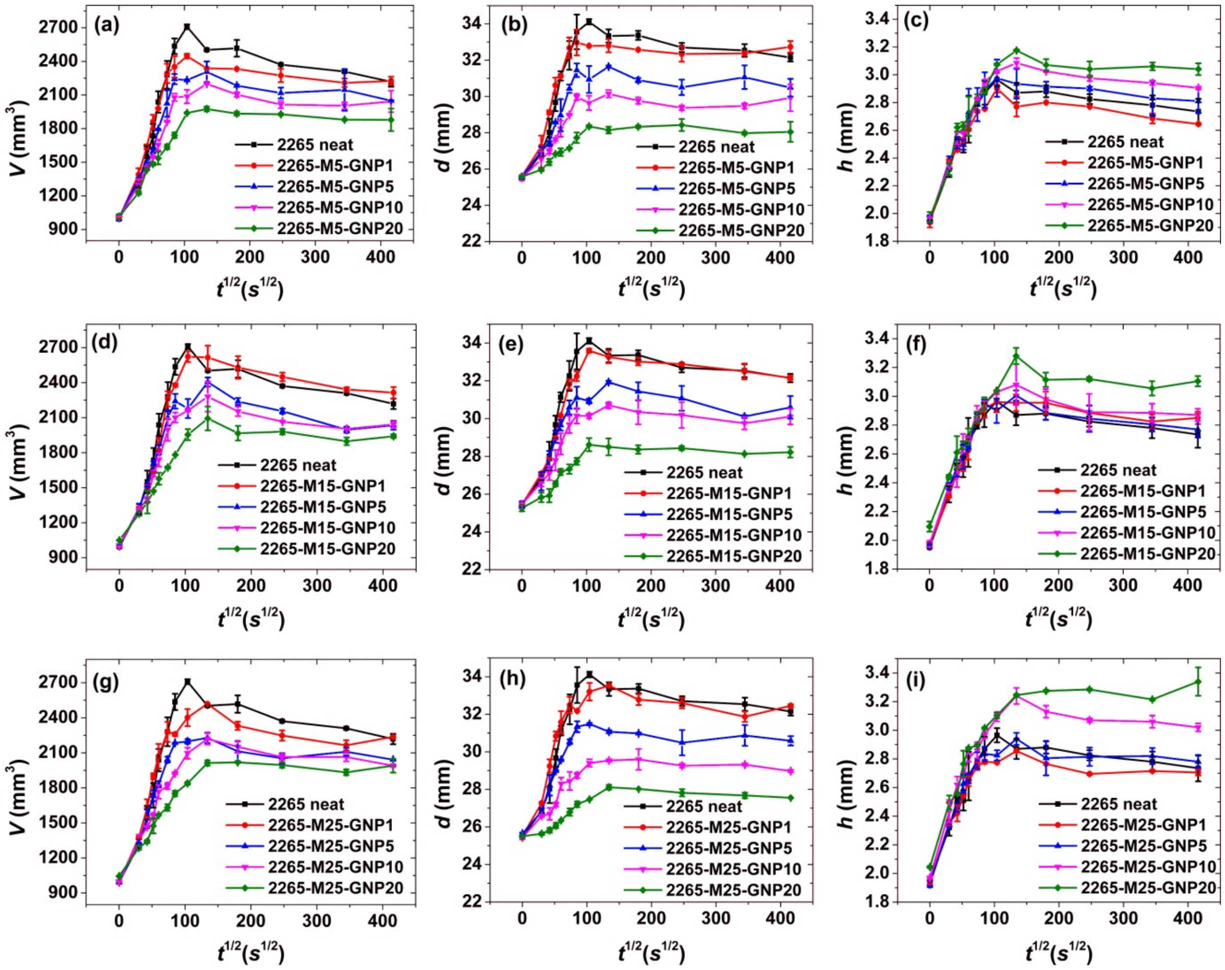

Figure S4. The geometric determination of all samples recorded at each intervals during the swelling tests: (a-c) volume, diameter and thickness of M5 GNP reinforced elastomers; (d-f) volume, diameter and thickness of M15 GNP reinforced elastomers; (g-i) volume, diameter and thickness of M25 GNP reinforced elastomers. The lines are guides to the eye.

S5. Anisotropic swelling – Flory-Rhener theory

The reinforcement of the graphene nanoplatelets in the elastomeric matrix in the swelling process in a solvent can be considered as mechanical constraint to the elastomer. The deformations of constrained materials during the swelling process are illustrated in the Figure S4, from the original size of the sample (left side) with diameter of d_0 and thickness of h_0 to the size of the sample at the equilibrium (right side) with diameter of d_e and the thickness of h_e.

At the equilibrium, the elastomer is constrained by the filler in the in-plane direction (diameter) as the blue arrows indicate and in the cross-plane direction (thickness) as the red-dash arrows show. Since the GNPs are well-oriented in the in-plane direction, the constraining force from the GNPs in the cross-plane directions is assumed to be 0 (the force illustrated by the red dashed arrows in the Figure S4 equals to zero).

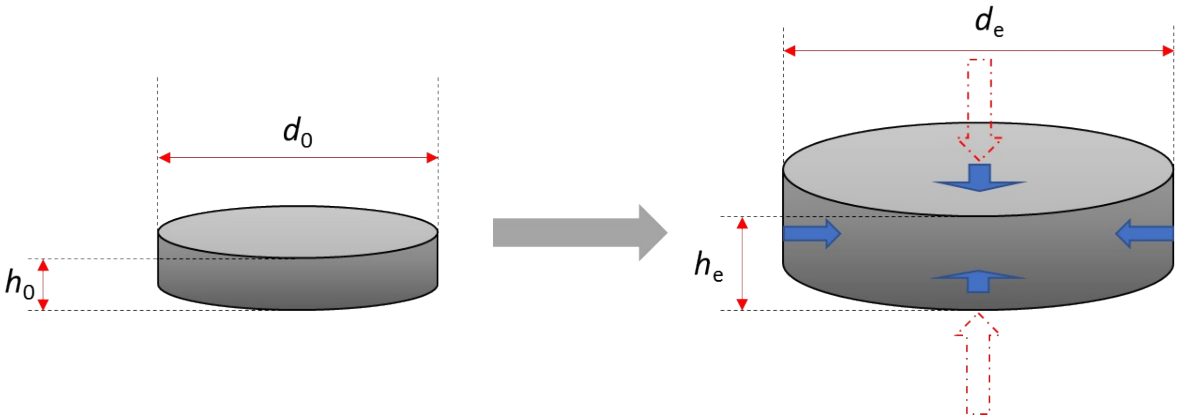

Figure S5. Schematic diagram of the swelling process of a composite sample from the unswollen state to the equilibrium swollen state under the constraining force generated by the GNPs from in-plane direction (blue arrows) and cross-plane direction (red dashed arrows). Since the GNPs are oriented in-plane, the force represented by the red-dashed equals to zero.

Based on the Flory-Rhener equation[1, 2] and Treloar's discussion[3] on bi-axially constrained elastomer in the process of swelling in liquid, the dependences of the swelling in the cross-plane and in-plane direction are respectively given by,

$$[\ln(1 - v_2) + v_2 + \chi v_2^2] + \frac{\rho V_1}{M_c}\left(\frac{h_e}{h_0}\right)^2 v_2 = 0 \tag{S1}$$

$$[\ln(1 - v_2) + v_2 + \chi v_2^2] + \frac{\rho V_1}{M_c({}^{d_e}/_{d_0})^4 v_2} = 0 \tag{S2}$$

Where v_2 is the volume fraction of the materials in the swollen gel, d_e/d_0 and h_e/h_0 are diameter and thickness swelling ratio respectively at the equilibrium, V_1 is molar volume of the solvent, ρ is the density of the neat polymer, M_c is the number average molecular weight of network chains of the polymer, which is related to the mechanical properties of the material and χ is a dimensionless parameter and dependent upon the polymer-solvent interaction.

The original Flory-Rhener equation for neat polymer under isotropic swelling at the equilibrium is given by,[3]

$$\rho V_1 \Big/ M_c \approx \left(\frac{1}{2} - \chi\right) v_{2\,\mathrm{neat}}^{\frac{5}{3}} \tag{S3}$$

In the equation (S3), the intrinsic properties of the polymer (ρ, M_c), solvent (V_1) and the polymer-solvent interaction (χ) can be determined by the volume swelling ratio at the saturation of the neat polymer ($1/v_{2\ \mathrm{neat}}$). Assuming that the introduction of the GNPs does not change the crosslinking density and combining equation S3 with the aid of expansion of the logarithm and neglecting higher powers of v_2, equations S1 and 2 become,

$$d_e/d_0 = ({}^{1}/_{v_{2\,\mathrm{neat}}})^{-5/12} \cdot ({}^{1}/_{v_2})^{3/4} \tag{S4}$$

$$h_e/h_0 = \left(1/v_{2\,\text{neat}}\right)^{5/6} \cdot \left(1/v_2\right)^{-1/2} \qquad \text{(S5)}$$

where $(1/v_2)$ is the swelling ratio of the volume for either neat polymer or nanocomposites. When the material is neat polymer, equations S4 and 5 give $d_e/d_0 = h_e/h_0 = (1/v_{2\,\text{neat}})^{1/3}$, which is for isotropic swelling. The products (d_e/d_0) and (h_e/h_0) are the respective swelling ratios of the dimension in the in-plane (diameter) and cross-plane (thickness) directions at the equilibrium, which is at the saturation of the swelling.

S6. Compositional characterisation

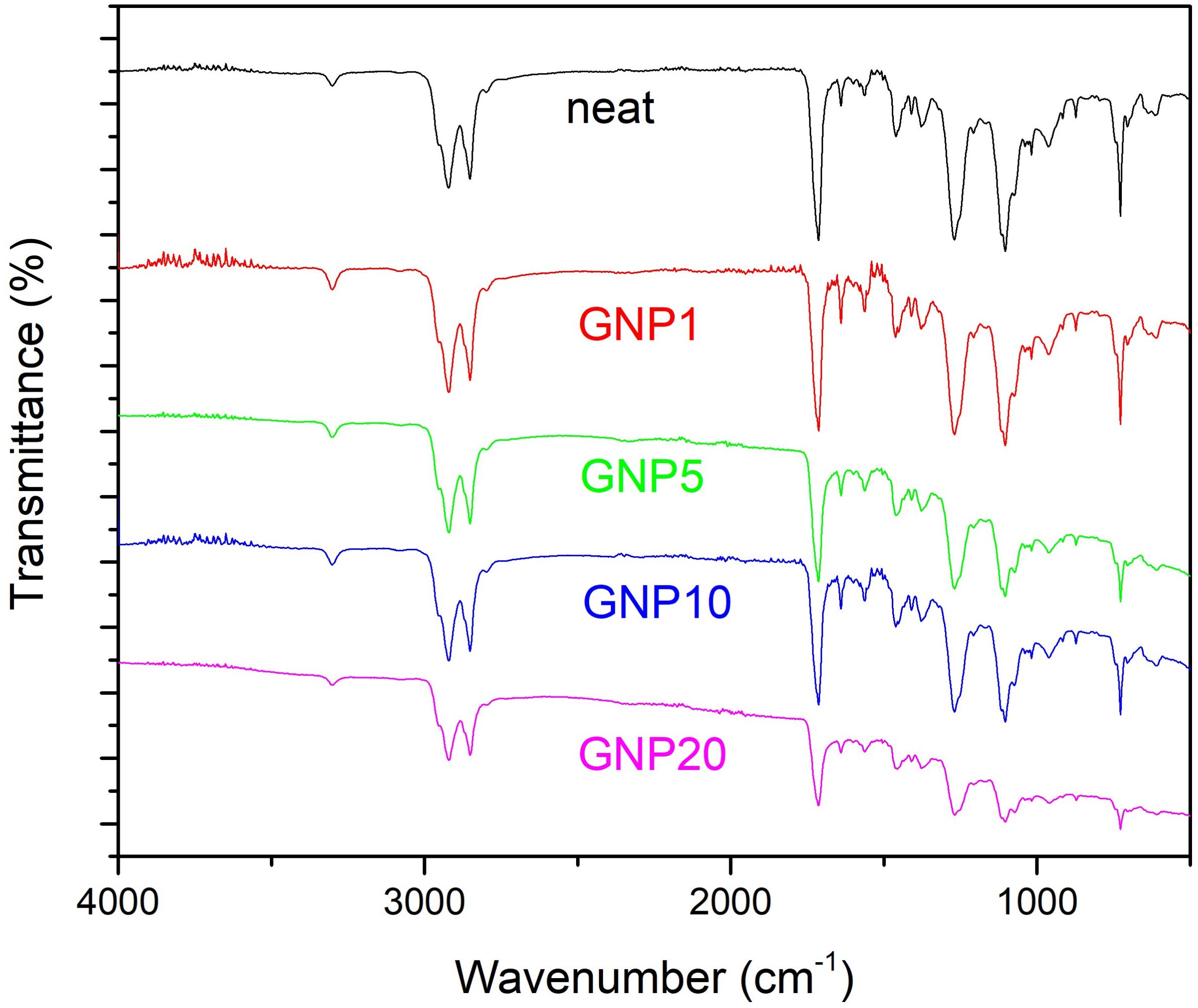

Figure S6. Representative FTIR spectrum for the elastomer nanocomposites at different loadings.

S7. Mechanical properties

The representative stress-strain curves for all the materials are shown in Figure S6. The related modulus obtained by linear fittings for the initial deformation of the materials are all listed in Table S2. All the results acquired are based 5 specimens for each sample. The stress-strain curves shown in Figure S6 represent the mechanical properties in the plane of the pressed elastomer sheet. As can be seen, due to the in-plane orientation of the GNPs, the modulus of the materials is increased significantly. There is a correlation between the modulus and the swelling ratios of the materials that is discussed in S7 below.

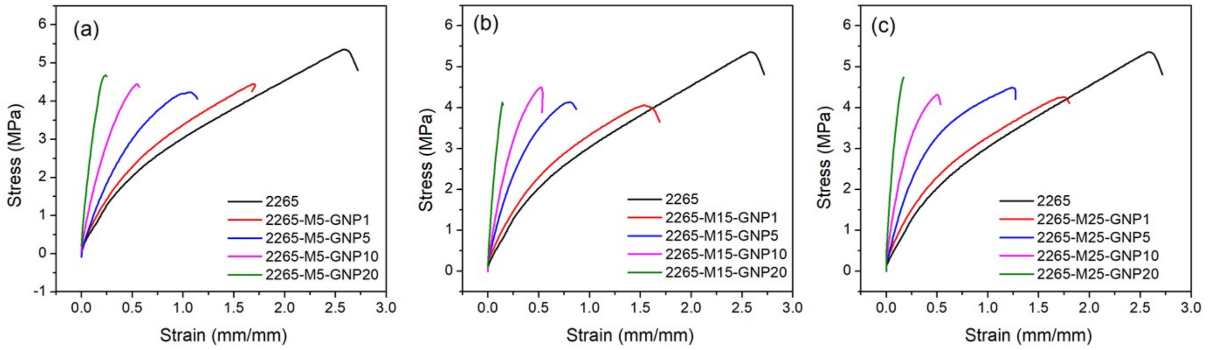

Figure S7. Representative stress-strain curved measure by tensile testing, for (a-c) M5, M15 and M25 reinforced thermoplastic elastomers.

Table S2. The modulus values obtained from tensile tests. The moduli were acquired by linear fittings on the stress-strain curves for the initial deformation of the samples.

Materials	Modulus (MPa)
2265	4.31 ± 0.11
2265-M5-GNP1	5.43 ± 0.20
2265-M5-GNP5	7.58 ± 0.13
2265-M5-GNP10	11.70 ± 0.40
2265-M5-GNP20	20.00 ± 0.42
2265-M15-GNP1	5.49 ± 0.17
2265-M15-GNP5	8.44 ± 0.32
2265-M15-GNP10	13.11 ± 0.74
2265-M15-GNP20	23.07 ± 0.72
2265-M25-GNP1	5.38 ± 0.36
2265-M25-GNP5	9.21 ± 0.32
2265-M25-GNP10	13.66 ± 0.74
2265-M25-GNP20	26.47 ± 0.72

S8. Correlations between modulus and swelling

It is believed that the anisotropy of the swelling is due to the anisotropy of mechanical properties, which results from the in-plane orientation of the nanoplatelets. The swelling of the materials in the solvents results from the osmotic pressure (Π) that is also called swelling pressure.[3] The osmotic (swelling) pressure (Π) from the solvent to the elastomers is given by, [3]

$$\Pi = -(\mathrm{R}T/v_1)\ln(p/p_0) \tag{S6}$$

where R is the gas constant, T is the Kelvin temperature, v_1 is the molar volume of the pure liquid, p is the vapour pressure of the liquid component in equilibrium with the mixture (swollen rubber) and p_0 is the saturation vapour pressure of pure liquid. The swelling pressure is dependent only upon the type of the solvent and defined as the pressure that keeps an elastomer swollen at equilibrium.[3] Therefore, the swelling pressure is independent upon the directionality of the measured samples and as such, we should have,

$$\Pi_{\parallel} = \Pi_{\perp} = E_{\parallel}\varepsilon_{\parallel} = E_{\perp}\varepsilon_{\perp} \tag{S7}$$

where $E_{\parallel}$ and $E_{\perp}$ are the uniaxial moduli of the nanocomposites parallel (x or y) and perpendicular (z) to the filler orientation (in-plane), respectively, and $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the corresponding strains at saturation of swelling. The swelling strains are,

$$\varepsilon_{\parallel} = \frac{d_{\mathrm{e}} - d_0}{d_0} \tag{S8}$$

and

$$\varepsilon_{\perp} = \frac{h_{\mathrm{e}} - h_0}{h_0} \tag{S9}$$

The modulus parallel to the filler orientation ($E_{\parallel}$) is related to the modulus values measured parallel to the rubber sheets, which can be considered as the modulus of the composites (E_{c}). The modulus perpendicular to the filler orientation ($E_{\perp}$) can be considered equal to the modulus of the neat matrix (E_{m}), since it was found that the GNPs did not constrain the swelling in the out-of-plane direction.

Combining equations (S7-9), we have,

$$\frac{E_c}{E_m} \approx \frac{E_{\parallel}}{E_{\perp}} \approx \frac{h_e/h_0 - 1}{d_e/d_0 - 1} \tag{S10}$$

The relation shown in equation (S10) is examined by a plot of [(h_e/h_0-1)/(d_e/d_0-1)] as a function of E_c/E_m in Figure S7. As can be seen, the datapoints lie on the linear plot of y=x, indicating the validity of equation (S10).

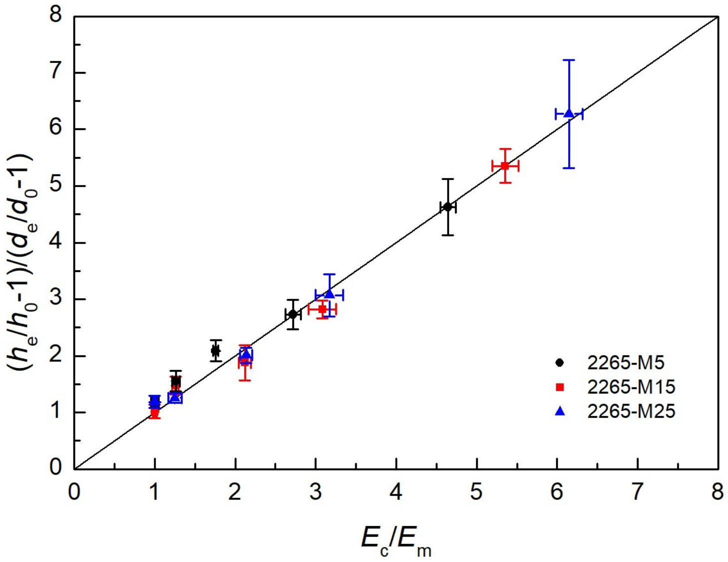

Figure S8. The swelling strain ratios [(h_e/h_0-1)/(d_e/d_0-1)] against the normalized modulus (E_c/E_m) obtained from tensile tests (Table S2) for all the samples.

Reference

1. P. J. Flory and J. Rehner Jr, *The Journal of Chemical Physics*, 1943, **11**, 521-526.

2. P. J. Flory and J. Rehner Jr, *The Journal of Chemical Physics*, 1943, **11**, 512-520.

3. L. R. G. Treloar, *The physics of rubber elasticity*, Oxford University Press, USA, 1975.