Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting Information for:

Advancing elastomer performance with dynamics bond networks in polymer-grafted single-chain nanoparticles: A molecular dynamics exploration

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Table of contents

1. MSD across varying quantities of functional groups:

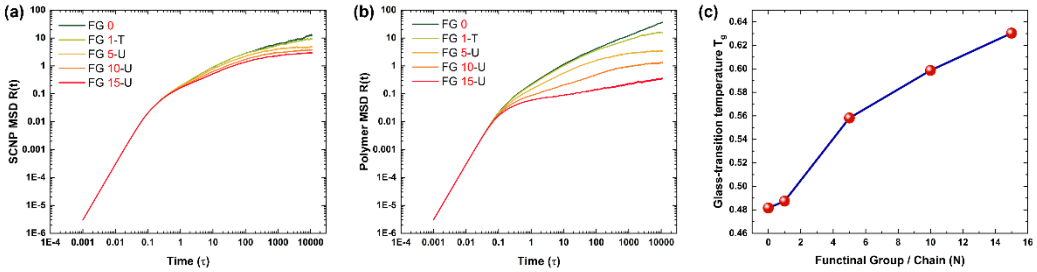

Figure S1. MSD of (a) soft SCNPs, (b) grafted polymer chains across varying quantities of functional groups, (c) variation of T_g with functional group quantity in polymer nanocomposites.

2. Calculation of glass transition temperature (T_g) for different samples

The temperature-volume method, which provides an accurate estimation of T_g by closely monitoring how the material's volume responds to temperature changes across different compositions, was used to calculate the T_g for FG 0, FG 1-T, FG 5-U, FG 10-U, FG 15-U, FG 15-C3, FG 15-C5, and FG 15-C15, as shown in Figure S2 panels (a) to (h).

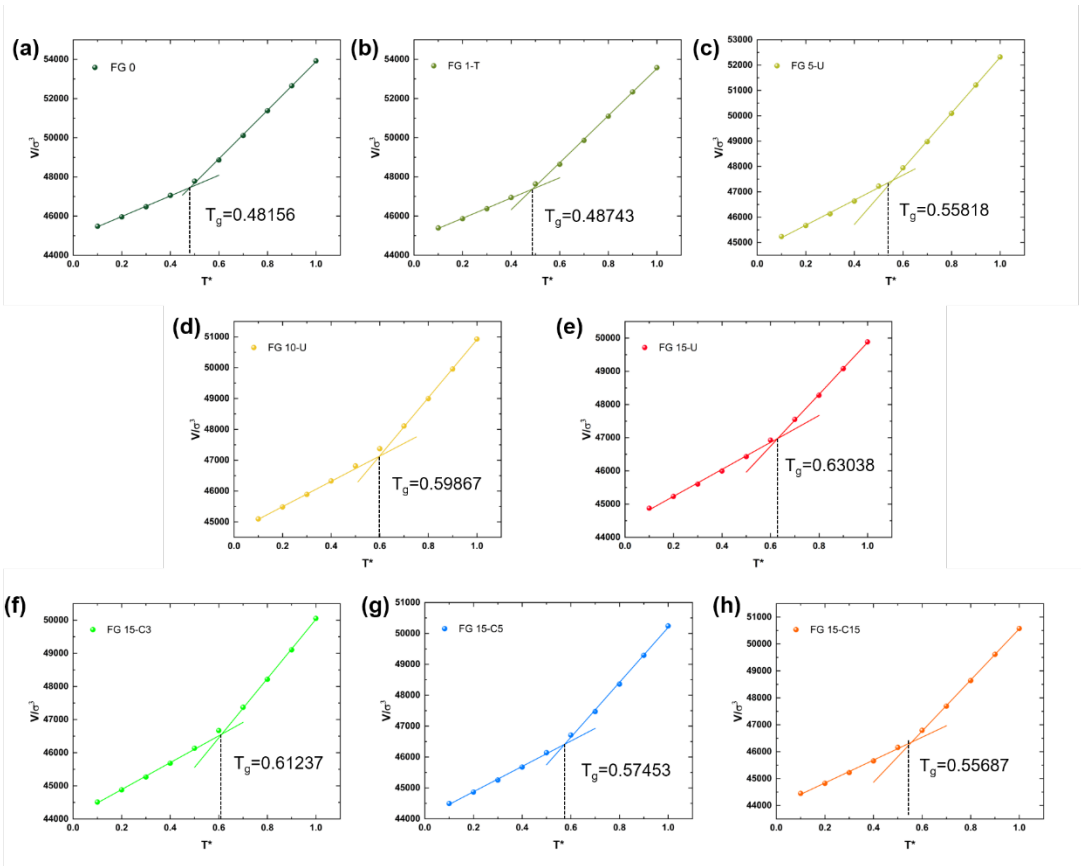

Figure S2. Variation of glass transition temperatures (T_g) across different functional group quantities and distributions in polymer nanocomposites: (a) FG 0, (b) FG 1-T, (c) FG 5-U, (d) FG 10-U, (e)

FG 15-U, (f) FG 15-C3, (g) FG 15-C5, (h) FG 15-C15.

3. Radius of gyration tensor G calculation details:

Each element of the radius of gyration tensor **G** is calculated via the following equations:

$$R_{\alpha\beta} = \frac{1}{N}\sum_{i=1}^{N}(\alpha_i - \bar{\alpha})(\beta_i - \bar{\beta}) \quad \text{(S1)}$$

Herein, N represents the number of monomers in the one soft SCNP. The symbols α, β, which can be x, y or z refer to the coordinates of the i-th monomer bead. Meanwhile, $\bar{\alpha}, \bar{\beta}$ correspond to the coordinates of the centroid of the soft SCNP. Subsequently, to glean more insights regarding the conformation of polymer chains, it's imperative to compute the principal moments (eigenvalues) of the Radius of Gyration Tensor **G**. This is achieved through eigenvalue decomposition by solving the characteristic equation:

$$\det(\mathbf{G} - \lambda\mathbf{I}) = 0 \quad \text{(S2)}$$

Solving this characteristic equation yields three eigenvalues, namely λ_x, λ_y, λ_z, which are the principal moments of the radius of gyration tensor.

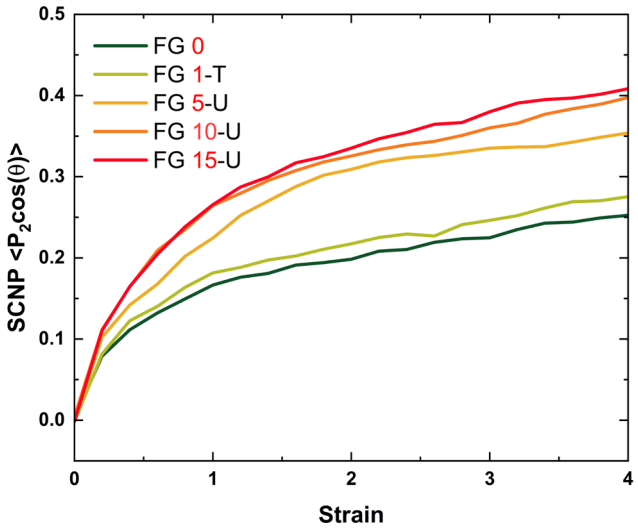

Figure S3. Variations in bond orientation within SCNPs in response to different quantities of dynamics functional groups on grafted polymer chains

4. Structural and dynamic responses under triaxial tensile testing of FG 1-T sample

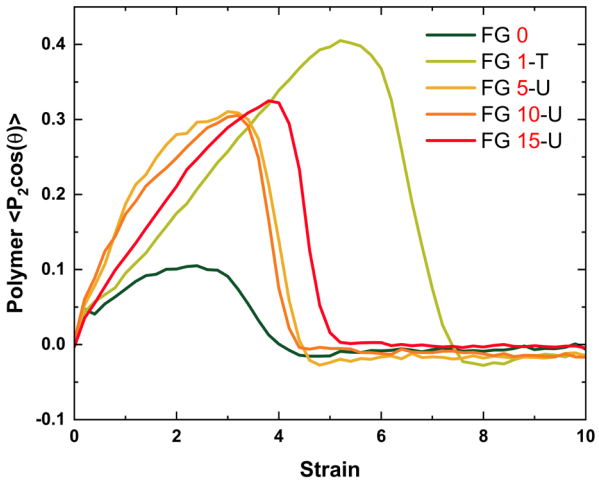

Figure S4. Grafted polymer bond orientation during triaxial tensile test with different dynamics group contents

In FG 1-T samples, the dynamic functional groups AFP-GSCNP and DFP-GSCNP are located at the outermost layer of the grafted polymer chains, particularly at the chain ends. This structural characteristic significantly influences the samples' behavior under strain, especially during triaxial tensile tests. At lower strains, the stress response of these samples closely resembles that of samples without dynamic functional groups (FG 0 sample), primarily due to stress originating from the entanglement of the chain segments themselves. However, as the strain increases, the stress behavior begins to deviate, with the interactions between the AFP-GSCNP and DFP-GSCNP functional groups at the chain ends becoming the primary stress contributors. This shift in stress source is crucial for understanding the unique stress-strain behavior observed in FG 1-T samples.

To elucidate the unique stress-strain characteristics of the FG 1-T sample, we employed the second-order Legendre polynomials equation for testing the orientation of the grafted polymer chains, as detailed in equation 9. The results, presented in Figure S3, indicate a higher $\langle P_2\cos\theta \rangle$ value for the FG-1T sample. Additionally, structural and dynamic analyses, encompassing factors such as T_g and MSD data, revealed that the grafted chains in the FG-1T sample, apart from the end functional groups, exhibit greater flexibility and fewer constraints. This inherent flexibility and lack of constraints in the network structure render the FG 1-T sample's network more prone to bending and twisting under tension. This sparse network structure potentially enhances the material's toughness and ductility, thereby necessitating higher strain values for the stress to drop to zero. The capability of bending and twisting contributes to the absorption of a portion of the stress, resulting in stress reduction to zero at higher strain values. In summary, the unique orientation and structural characteristics of the grafted polymer chains in the FG 1-T sample collectively account for its distinctive stress-strain behavior observed during triaxial tensile testing.

5. The asphericity factor for the uniaxial tensile test with

different number of dynamics groups on the grafted chain

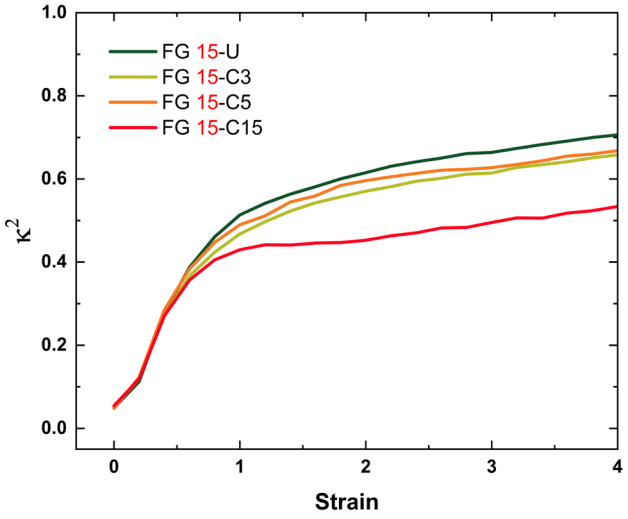

Figure S5. Asphericity factor κ^2 during uniaxial tensile test with different dynamics group distribution