Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Molecular Dynamics Simulation on Mechanical Properties of Natural-Rubber-Graft-Rigid-Polymer/Rigid-Polymer Systems

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1. The standard 12/6 Lennard-Jones (LJ) potential

The standard 12/6 Lennard-Jones (LJ) potential U_r (Eq. 1 in the main text) are used for non-bonded pairs of particles. The U_r at $r = 2^{1/6}$ is the global minimum, where the function changes the sign of slope (see Fig. S1). That is to say the interactions change from repulsion to attraction at $r = 2^{1/6}$.

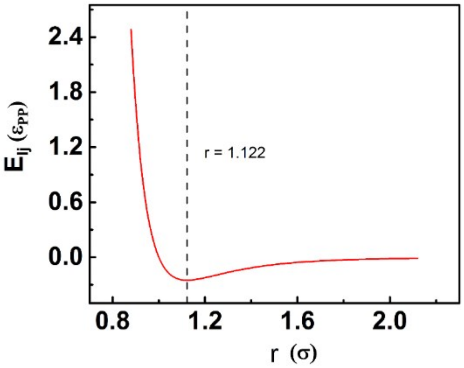

Fig. S1. Curve of E_{lj} with respect to r.

2. Energy changes in the equilibrium process

In the equilibrium process, we examined the temporal evolution of the morphologies and the total energy of systems. Fig. S2 shows the curve of total energy versus time of a typical system (N_{30}-g-$(R_3)_6/R_{10}$ with NR polymer beads : Rigid polymer beads = 1:1 and ε_{RR} = 5.0). It can be seen that the total energy drops first and then maintains a constant value with little fluctuation. After 1×10^7 steps, the total energy is stabilized and the morphology is not changed (insets of Fig. S2), and thus it can be considered that the system has reached equilibrium for a relative long time (5×10^7 steps).

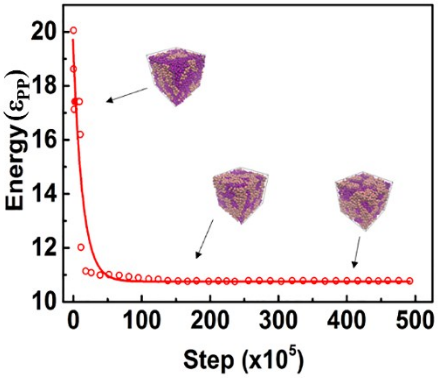

Fig. S2. Curve of energy as a function of step in the N_{30}-g-$(R_3)_6/R_{10}$ systems with NR polymer beads : rigid polymer beads = 1:1 and ε_{RR} = 5.0.

3. External effect of stretching velocities on mechanical properties of N_{30}-g-$(R_3)_6/R_{10}$ blend systems

Second-order Legendre[S1] polynomials P_2 was employed to further characterize the bond orientation of the systems, and the value of P_2 reflects the chain orientation. The results at various stain rates are shown in Fig. S3. P_2 increases continuously with increase in strain. However, the values of P_2 are almost the same in the five different strain rate systems, but a slightly larger in systems with higher strain rate during the tensile process. This indicates that systems with different strain rates have similar degree of bond orientation, which contributes similarly to the mechanical properties in terms of entropy loss.

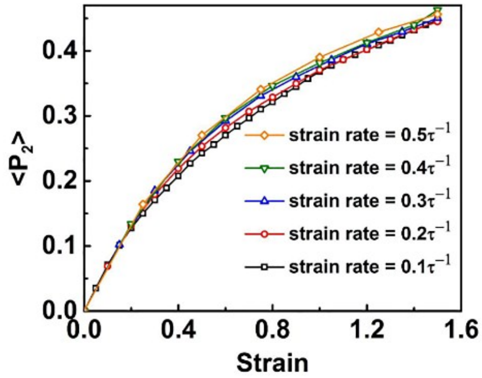

Fig. S3. Second-order Legendre polynomials P_2 at various strain rates from $0.1\tau^{-1}$ to $0.5\tau^{-1}$ for N_{30}-g-$(R_3)_6/R_{10}$ systems at $\varepsilon_{RR} = 5.0$.

4. Internal effects on mechanical properties of N_{30}-g-$(R_3)_6/R_{10}$ systems

4.1 Effects of FENE Potential on mechanical properties of N_{30}-g-$(R_3)_6/R_{10}$ systems

The modified finite extensive nonlinear elastic potential,[S2] namely FENE potential (Eq. 2 in the main text), was used to determine the interaction between the adjacent bonded polymer beads, which is the intramolecular interactions. k is the parameter to control the strength of the interactions. Fig. S4 shows the stress-strain curves for N_{30}-g-$(R_3)_6/R_{10}$ systems at various k; stress increases rapidly at the beginning of the tensile process, and then increases mildly at large strain for all various systems. Nevertheless, the tensile behaviors among different interaction strengths are nearly the same but noisy, indicating a reasonable fact that the mechanical property is not mainly determined by the intramolecular interaction but by the intermolecular interaction. Moreover, the curves of the systems with stronger intramolecular interactions show larger fluctuation, which means higher deviations.

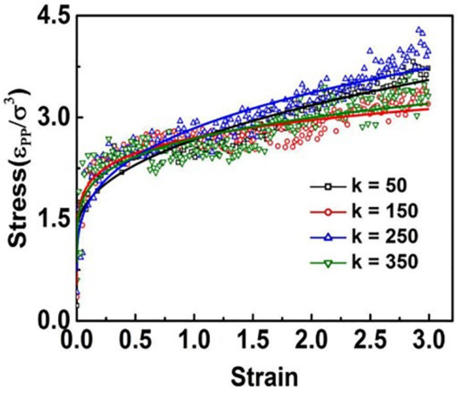

Fig. S4. Representative stress-strain curves for N_{30}-g-$(R_3)_6/R_{10}$ systems at various FENE parameter k.

4.2 Effect of nonbonding interaction strength of ε_{RR} on mechanical properties for N_{30}-*g*-$(R_3)_6/R_{10}$ systems

The non-bonded interaction within rigid polymer beads is the important factor in determining the mechanical properties relative to the bonded interaction. Representative stress-stress curves of N_{30}-*g*-$(R_3)_6/R_{10}$ blends at various ε_{RR} are shown in Fig. S5a. As ε_{RR} increases, the stress increases at the same strain, which rises more remarkable at large strain. As can be seen in Fig. S5b, P_2 increases with increasing strain, but it shows similar behaviors during the tensile process in systems with different ε_{RR}. This result suggests that with various ε_{RR}, systems have almost the same degree of bond orientation, which makes similar contributions to the mechanical properties.

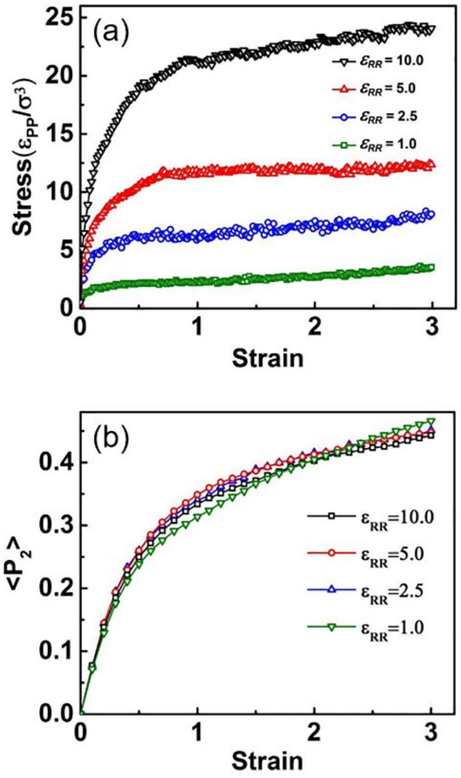

Fig. S5. (a) Stress-strain curves for N_{30}-*g*-$(R_3)_6/R_{10}$ systems at different ε_{RR} with strain rate of $0.2\tau^{-1}$. (b) P_2 as a function of strain for N_{30}-*g*-$(R_3)_6/R_{10}$ systems at various ε_{RR}.

4.3 Effect of rigid polymer proportion on mechanical properties for N_{30}-*g*-(R_3)$_6$/R_{10} systems

Stress-strain curves for various proportions of rigid polymer were shown in Fig. S6a. With the addition of rigid polymers, the stress increases continuously. However, when the proportion of rigid polymers further increases to 80%, the stress stops increasing and is about the same with that in the blends of 75% rigid proportion. The result suggests that the enhancement of the mechanical properties of the blends by addition of rigid polymers will be saturated. The effective bond length was calculated as shown in Fig. S6b, $l_{b,eff}$ increases gradually at small strain then has little changes at large strain during the tensile process. Also, the value of $l_{b,eff}$ was found to be smaller at the same strain in systems with more rigid polymers, which means that stronger attraction between numerous rigid polymer beads makes the average bond length shorter.

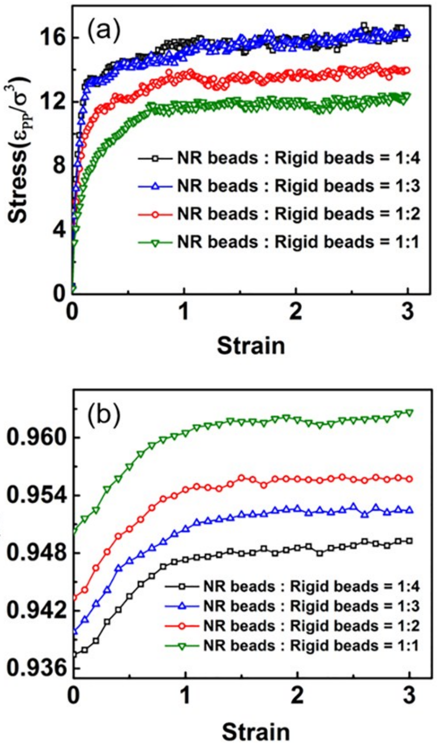

Fig. S6. (a) Stress-strain curves at different ratios of NR beads to rigid beads for N_{30}-*g*-(R_3)$_6$/R_{10} systems with strain rate = $0.2\tau^{-1}$. (b) $l_{b,eff}$ as a function of strain for N_{30}-*g*-(R_3)$_6$/R_{10} systems at various ratios of NR beads to rigid beads.

4.4 Effect of architecture parameters on mechanical properties for rigid-polymer-grafted-NR/rigid-polymer system

We studied the effects of architecture parameters in systems with the same molecular number in each type, which means we varied the length and the number of the graft chains by fixing the number of rigid molecules and rigid-polymer-grafted-NR molecules (180 rigid molecules and 150 rigid-polymer-grafted-NR molecules). Stress-strain curves were shown in Fig. S7a. Stress increases rapidly with increasing strain at small strain. Larger values of the stress were found at small strain in systems where NR-graft-rigid-polymer molecules have more graft chains. However, stress increases continuously in systems where NR-graft-rigid-polymer molecules have longer graft chains. Moreover, almost the same values of the stress were found at large strain in systems in which NR-graft-rigid-polymer molecules have the same length of graft chains, suggesting that the increase in stress at large strain is mostly contributed by the length of the graft chains, while that is contributed by the number of graft chains at small strain. As shown in Fig. S7b, P_2 increases with increasing strain. Moreover, larger values of P_2 were found in systems at large strain where NR-graft-rigid-polymer molecules have longer graft chains, which exhibits larger degree of bond orientation during the tensile process. From Fig. S7c, we can see that $l_{\mathrm{b,eff}}$ increases with increasing strain at small strain and then has slight increases at large strain in the systems where NR-graft-rigid-polymer molecules have shorter graft chains. Moreover, durative increases in $l_{\mathrm{b,eff}}$ were found in systems in which NR-graft-rigid-polymer molecules have longer graft chains, suggesting that increase in stress at large strain is contributed from the length of graft chain, which causes large increase in entropy loss in the form of $l_{\mathrm{b,eff}}$. Moreover, the values of $l_{\mathrm{b,eff}}$ is small in systems where NR-graft-rigid-polymer molecules have longer of greater number of graft chains. This suggests that larger number of graft chains or longer graft chains in a NR-graft-rigid-polymer will lead to a system with more rigid polymers. And rigid polymer has stronger attractions, which causes shortening of average length of the bonds. As can be seen in Fig. S7d, ΔE_{pair} increases rapidly to the plateaus then has slight changes at large strain during the tensile test. Moreover, we found that the height of the curve is determined by the number of graft chains in a NR-graft-rigid-polymer, and larger values of ΔE_{pair} were found in systems in which NR-graft-rigid-polymer molecules have more graft chains. This demonstrates that the contribution of enthalpy gain in the form of ΔE_{pair} to the increase in stress is dominated by the number of the graft chains in a NR-graft-rigid-polymer at small strain. The increases in both entropy loss and enthalpy gain contribute to the increase in stress at small strain, while larger entropy loss is caused by the continuous increase in $l_{\mathrm{b,eff}}$, which leads to the increase in stress at large strain.

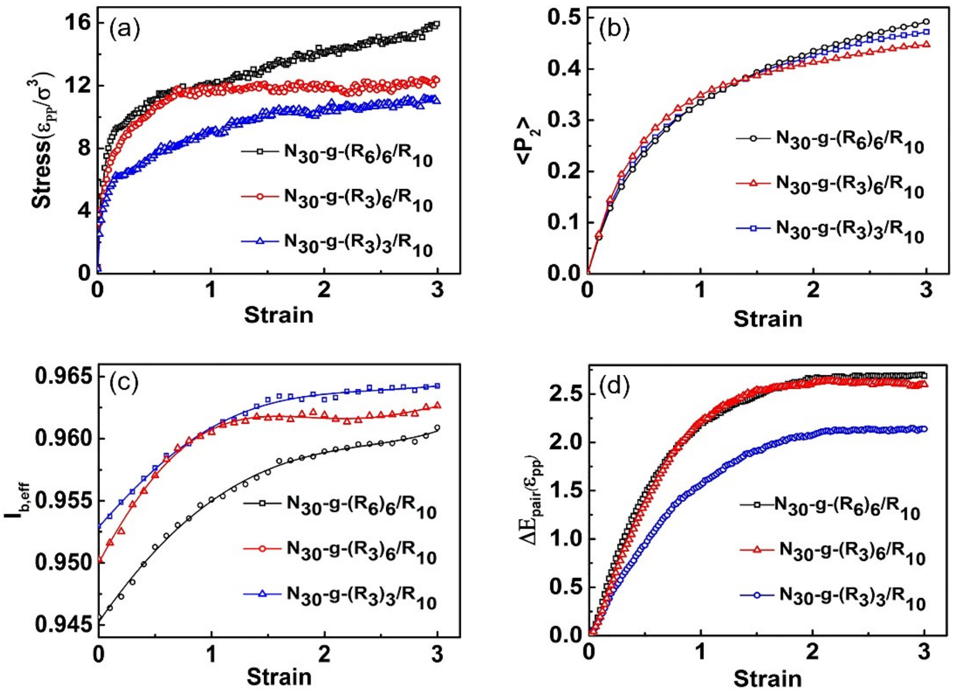

Fig. S7. (a) Stress-strain curves for various architecture parameters in systems with fixed molecular numbers in each type. (b) The bond orientation P_2 versus strain for various architecture parameters. (c) $l_{\mathrm{b,eff}}$ for various architecture parameters with respect to strain. (d) ΔE_{pair} as a function of strain for various architecture parameters.

Fig. S8 shows P_2 with respect to strain for various architecture parameters in systems with fixed 9000 polymer beads. P_2 increases with increasing strain, and almost the same values of P_2 in different systems were found at small strain. Furthermore, larger values of P_2 at large strain were found in the systems where NR-graft-rigid-polymer molecules have longer graft chains; however, as for the systems where NR-graft-rigid-polymer molecules have the same length of the graft chains, larger value of P_2 were found in which NR-graft-rigid-polymer molecules have small number of graft chains. It means that the blends where NR-graft-rigid-polymer molecules have fewer or longer graft chains have larger degree of bond orientation during the tensile process.

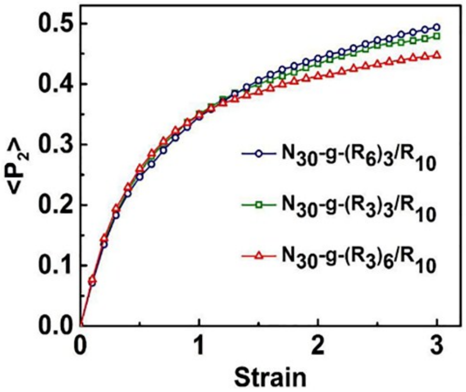

Fig. S8. P_2 as a function of strain for various architecture parameters in systems with constant number of polymer beads (9000).

5. The behaviors of the effective bond length at small strain for blend systems

The relationship of $l_{\mathrm{b,eff}}$ and strain at small strain (0~0.1) are also examined and shown in Fig. S9. It can be seen that the changes of $l_{\mathrm{b,eff}}$ for the two systems at small strain (<0.04) are close, and thus the systems of N_{30}-g-$(R_3)_6/R_{10}$ and N_{30}/R_{10} have the same stress-strain behavior at small strain (<0.04).

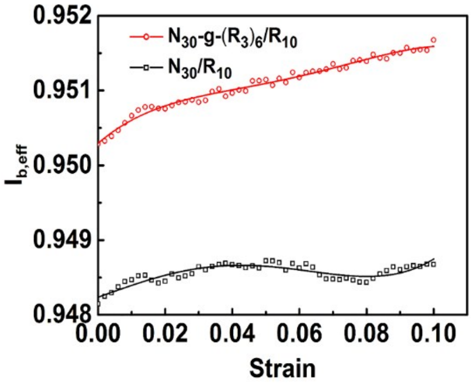

Fig. S9. $l_{\mathrm{b,eff}}$ as a function of the strain at small strain (0~0.1).

References

S1 J. Liu, Y. Wu, J. Shen, Y. Gao, L. Zhang and D. Cao, *Phys. Chem. Chem. Phys.*, 2011, **13**, 13058-13069.

S2 J. Liu, S. Wu, L. Zhang, W. Wang and D. Cao, *Phys. Chem. Chem. Phys.*, 2011, **13**, 518-529.