Electronic Supplementary Material (ESI) for Soft Matter

Modeling Polymer Grafted Nanoparticle Networks Reinforced by High-strength Chains

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Supplementary Information

In this study, grafted polymers on neighboring nanoparticles can form a link between the particles through functional groups at the chain ends. Here, we validate our assumption that if the bond formed between the two polymer arms has an energy of $100\,k_B T$, then the link can be represented by an unbreakable chain within the networks. Figure S1 shows histograms of the strain at break, ε_b, and toughness, W, from our simulations of stretching the chains at a fixed velocity ($v = 0.001 v_0$); the plots are for networks containing permanent bonds at $P_p = 1$ and $P_n = 0.15$ of either unbreakable chains or polymers connected by high-strength bonds ($100\,k_B T$). These histograms show that the distributions of the strain at break and toughness are very similar for these two different scenarios; even the average values and standard deviation ranges are comparable for the two cases. We emphasize this similarity through the use of Weibull statistics.[S1] Namely, we calculate the Weibull probability, P_b, which is obtained using the Bernard and Bos-Levenbach approximation.[S2] For example, for the strain at break, we determine the probability

$$P_b(\varepsilon_b = \varepsilon_b{}^j) = \frac{j - 0.3}{N_{\text{test}} + 0.4}, \tag{1}$$

where $\varepsilon_b{}^j$ is the strain at break for the j th sample of the ordered set and N_{test} is the total number of samples. For comparison, we added data for samples characterized by $P_p = 1.15$ and $P_n = 0$ (i.e., the system does not encompass either the unbreakable or the high-strength bonds). For each set of data, we also display the curve indicating the fit of the data to the Weibull probability in eq. (1). The plots in Fig. S2 clearly show that networks with unbreakable chains produce similar fitting curves to those with high-strength ($100\,k_B T$) bonds, and both sets display a pronounced improvement over networks that do not encompass either of these connections.

We repeated the analysis described above on samples with a greater probability of unbreakable chains or high-strength ($100\,k_B T$) bonds so that the system was characterized by $P_n = 0.3$. At this of value of P_n, the number of unbreakable chains are close to the percolation threshold; in our set of 40 runs, the chains formed percolating networks in seven of those cases. Figure S3 shows that for these $P_n = 0.3$ cases, there is a difference between unbreakable chains and high-strength bonds for the strain at break and toughness. Figure S4 also shows that the networks with unbreakable chains produce more samples that survive at high strains than the samples with high-strength bonds. This behavior is due to the rare failures of high-strength bonds when subjected to extreme strain (as displayed in Fig. 2 within the main article). The high-strength bonds do, however, provide a significant improvement in ductility and strength relative to the networks characterized by $P_p = 1.3$ and $P_n = 0$.

References

S1. B. R. Lawn, *Fracture of brittle solids*, 2nd ed., Cambridge University Press, New York, 1993.

S2. A. Bernard, and E. C. Bos-Lovenbach, *Statistica*, 1953, **7**, 163-173.

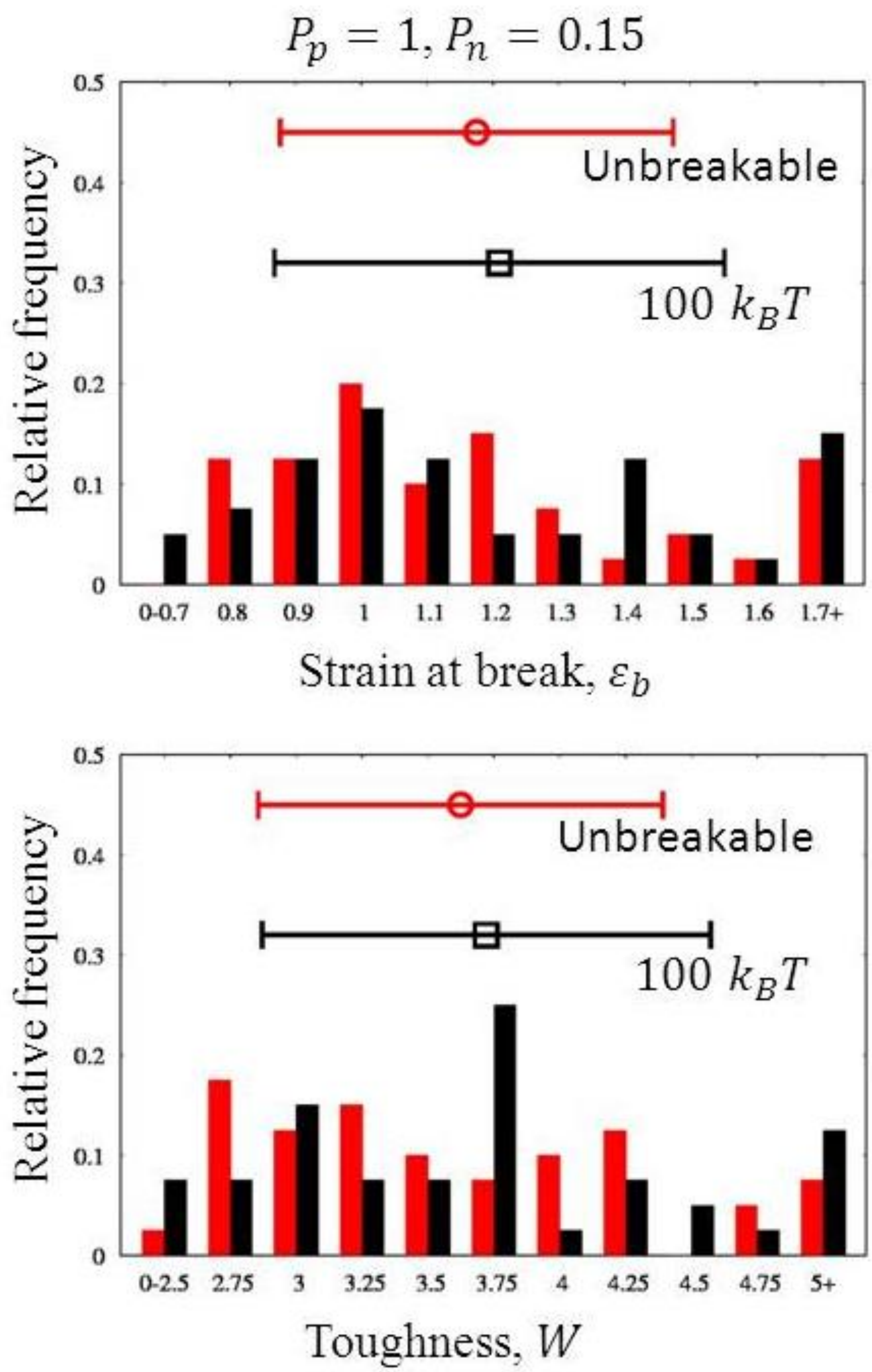

Fig. S1. Histograms of the (a) strain at break and (b) toughness for two equivalent systems with $P_t = 1.15$, composed of permanent bonds at $P_p = 1$ and the unbreakable chains (red) or high-strength connections with bond energy $100 k_B T$ (black) both introduced at $P_n = 0.15$. The average value and standard deviation obtained according to the Weibull statistics is shown for each distribution.

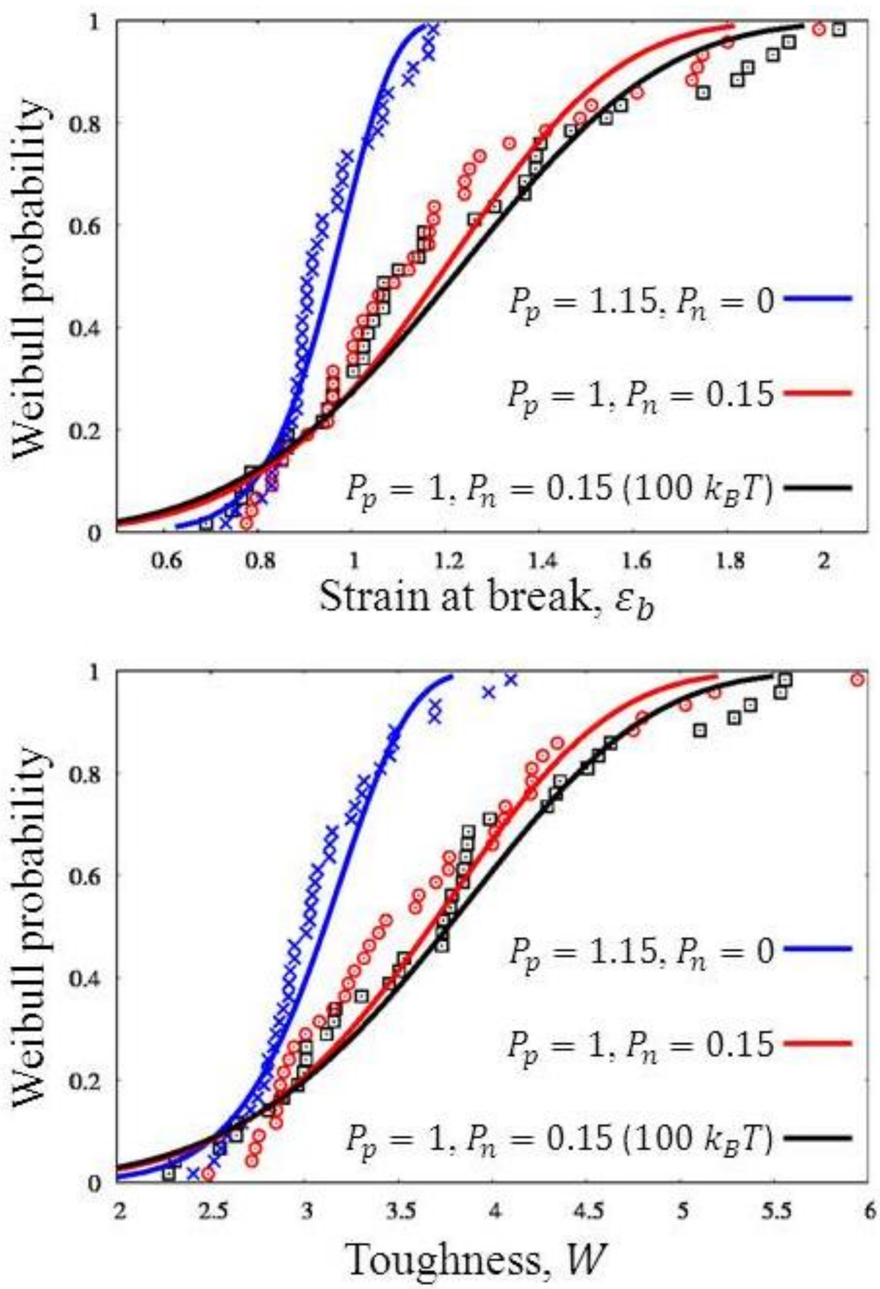

Fig. S2. Plots of 40 data points in ascending order for three different cases displaying: (a) strain at break and (b) toughness versus the calculated Weibull probability, as well as the associated fitting curves. One set comprises networks (blue crosses) with permanent bonds at $P_p = 1.15$ and no unbreakable chains $P_n = 0$. The other sets relate to networks with permanent bonds at $P_p = 1$ and either unbreakable chains (red circles) or high-strength connections with bond energy $100\,k_BT$ (black squares) both at $P_n = 0.15$.

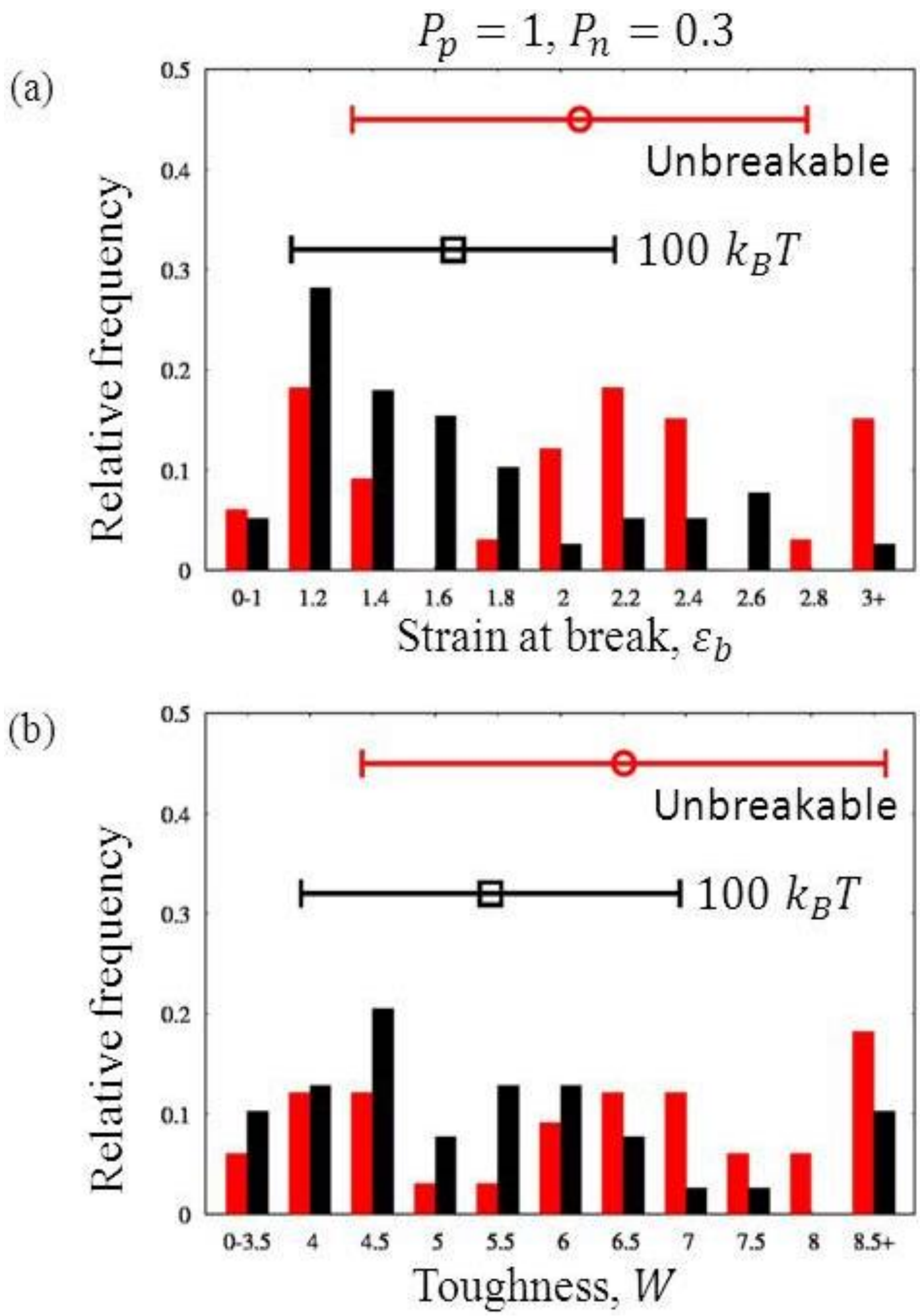

Fig. S3. Histograms of the (a) strain at break and (b) toughness for two equivalent systems with $P_t = 1.3$, composed of permanent bonds at $P_p = 1$ and the unbreakable chains (red) or high-strength connections with bond energy $100\,k_B T$ (black) both introduced at $P_n = 0.3$. The average value and standard deviation obtained according to the Weibull statistics are shown for each distribution.

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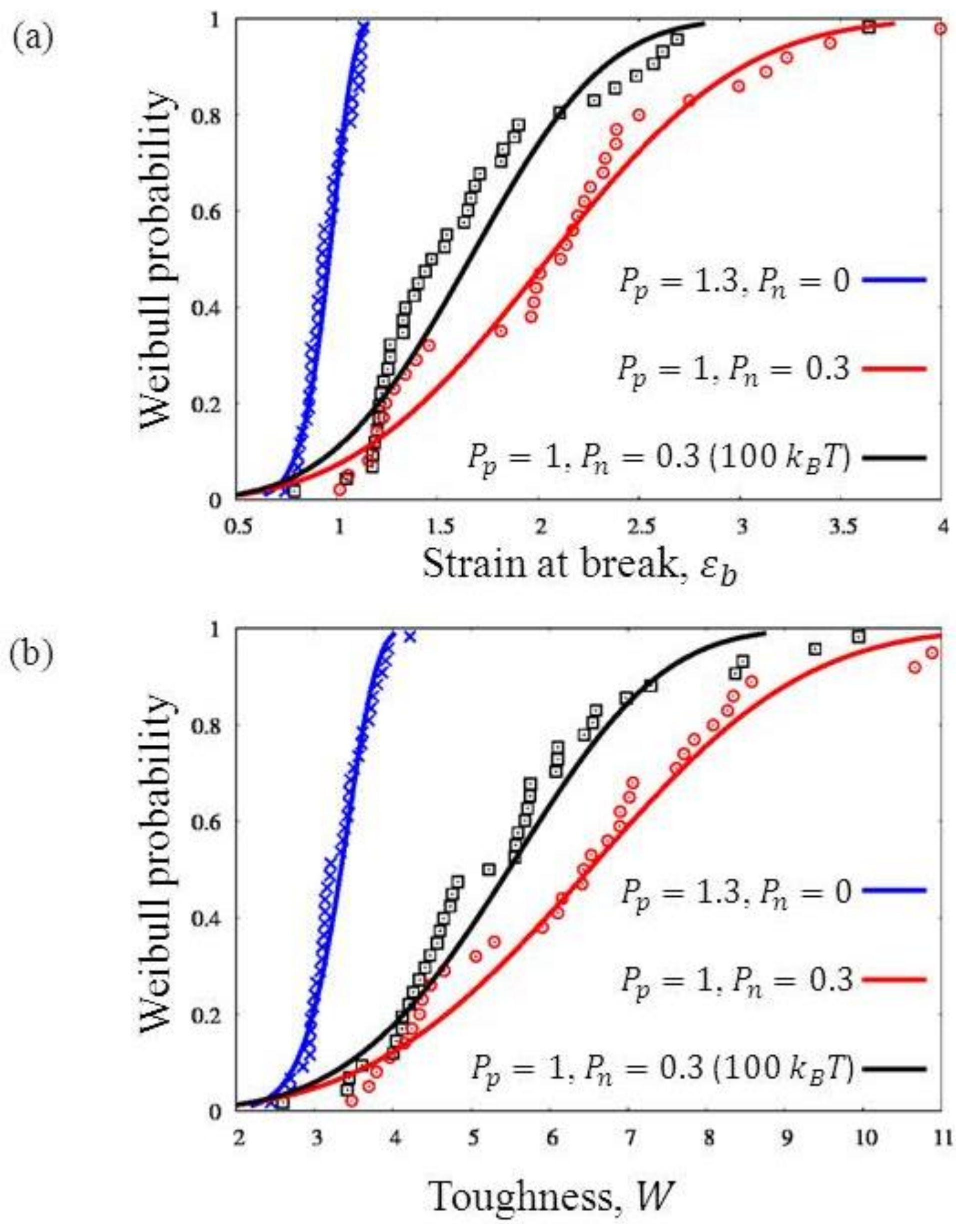

Fig. S4. Plot of 40 data points in ascending order (33 in the case of $P_p = 1$, $P_n = 0.3$ (red circles) due to percolations) for three different sets displaying: (a) strain at break and (b) toughness versus the calculated Weibull probability, as well as including the associated fitting curves. One set comprises networks (blue crosses) with permanent bonds at $P_p = 1.3$ and no unbreakable chains $P_n = 0$. The other sets relate to networks with permanent bonds at $P_p = 1$ and either unbreakable chains (red circles) or high-strength connections with bond energy $100 k_B T$ (black squares) both at $P_n = 0.3$.