MODELING THE RESPONSE OF DUAL CROSS-LINKED NANOPARTICLE NETWORKS TO MECHANICAL DEFORMATION

B. V. S. Iyer¹, I. G. Salib¹, V. V. Yashin¹, T. Kowalewski², K. Matyjaszewski², A. C. Balazs¹*

¹ Department of Chemical & Petroleum Engineering, University of Pittsburgh, Pittsburgh, USA, ² Department of Chemistry, Carnegie Mellon University, Pittsburgh, USA

* Corresponding author (balazs@pitt.edu)

1 Introduction
Advances in the grafting of polymer chains onto nanoparticles now permit significant control over the type and number of chains that can be anchored. Through the appropriate functionalization of these grafted chains, the coated nanoparticles can be interconnected into extensive networks. Recent studies have revealed that these nanoparticle networks can exhibit remarkable mechanical properties [1]. There are, however, few theoretical or computational models [2,3], that can provide useful guidelines for tailoring the properties of the functionalized chains to yield the desired mechanical properties in networks of polymer grafted nanoparticles (or “PGNs”).

The problem becomes particularly challenging due to a number of issues that must be addressed in designing an advantageous PGN network. For instance, while conventional soft nanogels provide a useful degree of elasticity, the polymers grafted onto the rigid nanoparticles must now impart the desired flexibility. Furthermore, the grafted polymers must be functionalized with the appropriate reactive groups in order to achieve an effective dual cross-linking. These constraints introduce a number of design variables, such as the length of the grafted chains and the interaction energies between reactive groups that play an important role in dictating the overall mechanical behavior of the composite.

The appropriate computational models would greatly facilitate the design of such hybrids materials. Such computational studies are challenging because all the relevant length and time scales should be captured in one specific model. Namely, the model must span a range of architectural features and temporal events. Herein, we develop an approach that encompasses the essential features to establish guidelines for tailoring the strength and toughness of PGN networks [4].

2 Model & Simulation Methodology
We develop a hybrid computational model for the behavior of a network of cross-linked polymer-grafted nanoparticles (PGNs). The individual nanoparticles are composed of a rigid core and a corona of grafted polymers that encompass reactive end groups (Fig 1). With the overlap of the coronas on adjacent particles, the reactive end groups can form permanent or labile bonds, which lead to the formation of a “dual cross-linked” network (Fig 1). To capture these multi-scale interactions, our approach integrates the essential structural features of the polymer grafted nanoparticles, the interactions between the overlapping coronas, and the kinetics of bond formation and rupture between the reactive groups on the chain ends.

Our system consists of a swollen network of cross-linked polymer-grafted nanoparticles (PGNs); the solvent is assumed to be a good solvent for the polymer chains. These PGNs are cross-linked by a combination of strong or “permanent” bonds and labile bonds to form an extended network. The rigid core of each nanoparticle has a radius $r_0$. The grafted polymers form a corona of stretchable chains around the nanoparticles; the thickness of this corona is given by $H = q r_0$. We assume that the chains within the corona are in the semi-dilute regime. In the ensuing studies, all the length scales in the system are given with respect to the core radius $r_0$ and hence, we consider a PGN of core radius unity and a corona thickness $q$.

The interaction between two PGNs is modeled through a sum of interaction potentials and is given by $U_{\text{int}} = U_{\text{rep}} + U_{\text{coh}} + U_{\text{link}}$. The first term, $U_{\text{rep}}$, characterizes the repulsive interactions between the grafted nanoparticles which decays exponentially at large separations and exhibits a logarithmic growth when the particles are brought close to each other [5]. The second term, $U_{\text{coh}}$, in the potential describes the attractive cohesive interaction between the coated particles and chosen such that it is constant for small values of separation between the particles but balances the repulsion at the edges of the corona to allow for overlap between neighboring coronas [5]. The final term, $U_{\text{link}}$, in the potential describes the attractive interaction [6] between the
particles linked by the bonded polymer arms and depends on the number of bonds, \( N_b \), formed between the given pair of particles.

The number of bonds formed, \( N_b \), depends on the maximum number of bonding pairs, \( N_{\text{max}} \), available in the corona overlap volume. We estimate the value of \( N_{\text{max}} \) by making the simplifying assumption that there is negligible distortion of the two coronas when they overlap. Then, purely geometric considerations yield the following expression [4]:

\[
N_{\text{max}}(R) = \left( \frac{f}{2} \right) \left[ 1 - R / (2(1 + q)) \right],
\]

where \( f \) is the total number of grafted polymer arms, \( q \) is the thickness of the corona and \( R \) is the center-to-center distance between two particles.

While \( N_{\text{max}}(R) \) corresponds to the maximum number of bonds that can be formed between two nanoparticles, the actual number of bonds formed, \( N_b \), depends on the number of bonding pairs available in the corona overlap volume, and on the rates of formation and rupture of individual bonds. The rate of formation depends on the probability of contact of two chain ends that, in turn, depends on the free-end distribution in the corona. In order to calculate the probability of contact \( P_c(R) \), we introduce the chain end distribution function \( g(r) \), which is the probability distribution function for finding a chain end at the distance \( r \) from the center of the nanoparticle. The distribution function \( g(r) \) is obtained from self-consistent field theory [7] and normalized as [4]:

\[
\int g(r) 4 \pi r^2 dr = 1
\]

The probability of contact, \( P_c(R) \), is determined by integration of the product of the individual free-end distributions in each corona over the volume of overlap [4]:

\[
P_c(R) = \int_{\text{overlap}} g(|R - r|) g(|r|) dr
\]

The evolution equation for the number of bonds can then be written as [4]:

\[
\frac{dN_b}{dt} = -k_f N_b + P_c(R) k_f [N_{\text{max}}(R) - N_b]^2,
\]

At the individual bond level, we use the Bell model [7] to describe the rupture and re-formation of bonds due to thermal fluctuations. In accordance with the Bell model, the rupture rate constant, \( k_{fr}^{(p,f)} \), is an exponential function of the force applied to the bond and is given by \( k_{fr}^{(p,f)} = k_{fr_0}^{(p,f)} \exp(\gamma_0 F) \), where \( k_{fr_0}^{(p,f)} = v^{(p,f)} \exp(-U_0^{(p,f)}/k_BT) \) is the rupture rate in the zero force limit that depends on the energy barrier \( U_0^{(p,f)} \) separating the bound and the free states for the permanent and labile bonds. In general, the rate constant of bond formation decreases under an applied force \([8]\). The force due to chain extension, however, only affects the rate constants \( k_{fr}^{(p,f)} \) and \( k_f^{(p,f)} \) at sufficiently large separations between a pair of polymer grafted nanoparticles. At the latter separations, the coronas do not overlap, so the total rate of labile bond formation is zero. Hence, for the sake of simplicity, we neglect the dependence of the rate constant of bond formation on force and consider it to be constant, \( k_{fr_0}^{(f)} \). We note that it is only the labile bonds that can reform after breaking; the permanent bonds can only break.

The dynamics of the system is assumed to be in the overdamped regime, with the motion of each particle governed by the equation \( \dot{x} = F/m \), where \( m \) is the mass and \( F \) is the total force on the polymer grafted particle. The total force acting on a particle can be written as \( F = -U_{\text{rep}} / \dot{x} + F_{\text{ext}} \), where \( F_{\text{ext}} \) is the external force acting on the edge particles of the particle array (see Fig 1b). This equation is solved numerically in two steps since the polymer spring force (within the expression for \( F_{\text{tot}} \)) in the dynamic equation depends on the number of bonds between particles and consequently, on the evolution of the chemical kinetics given by eq. (4). In the first step, we determine the number of bonds at any given time, \( N_b(t) \), by numerically solving eq. (4) through an explicit Euler scheme with a time step of \( \Delta t = 10^{-2} T_0 \), where \( T_0 \) is the unit of time in the simulation. Note that the numerical evolution of eq. (4) yields a real number, whereas the number of bonds \( N_b(t) \) should take discrete integer values. In order to determine the integer value, we compare the fractional part of the numerical result, \( \{N_b(t)\} \), with a random number \( \xi \) distributed uniformly between 0 and 1. If \( \{N_b(t)\} < \xi \), then we truncate the result; otherwise, we increment the integer part of the result by 1. In the second step, we use this value for the number of bonds to calculate the spring force in the dynamic equation and integrate numerically the resulting equation using a fourth-order Runge-Kutta algorithm with a time step of \( \Delta t = 10^{-2} T_0 \).

The initial state of the system is generated using the following five-step procedure. In the first step, the nanoparticles are placed in an array such that their centers are separated by a horizontal spacing of \( 1.8(1 + q) \) and a vertical spacing of \( 1.62(1 + q) \).
with a horizontal offset position of $0.855(1+q)$ between adjacent rows. In the second step, we hold the sample in the initial configuration for $4000$ $T_0$ units of time to allow for the formation of the labile bonds. In the third step, we equilibrate the sample for a time $6000$ $T_0$, during which the stressed labile bonds are broken and new bonds are formed between the adjacent PGNs according to eq.(4). In the fourth step, we establish the permanent bonds with the probability $P$. In this step, if two particles are linked with $N_k$ bonds, then with the probability $P_k$, one of the bonds is designated as “permanent”, so that the two particles become linked with $(N_k-1)$ labile bonds and one permanent bond. In this fifth step, the resultant sample composed of a dual-network of permanent and labile bonds is equilibrated for $10^4T_0$ and then subject to tensile deformation by stretching at a constant velocity of 3.55 nm/s. The latter value of velocity is similar to that used in single molecule pulling experiments [9].

In the ensuing simulations, we consider a particle of core radius $r_0 = 50$ nm with $f = 156$ polymer chains grafted onto its surface. The value of $f$ was chosen to satisfy the assumption that the corona chains are in the semi-dilute regime. The value of $f$ is used to determine the strength of repulsion and extent of bond formation between any two interacting particles. The cohesive interaction counteracts the repulsive forces at the corona edge. It is important to note that if the cohesive interactions are not taken into account, the equilibrium state of the pair of PGNs corresponds to no corona overlap and no labile bonds.

The motion of the particle in the overdamped regime is determined using the mobility computed as the inverse of Stokes drag, $\mu = \frac{6\pi\eta r_0(1+q)}{}^{-1}$, on a particle of radius $r_0(1+q)$ in a viscous fluid of viscosity $\eta = 0.894$ Pa $\times$ s (viscosity of glycerol).

In simulating bond kinetics, we fix the bond energy of the permanent bonds to be $U_{0}^{(p)} = 45k_B T$ and vary $P$ in the range $0 \leq P \leq 1$. Note that at $P=1$, each nanoparticle is interconnected by one permanent bond and at $P=0$, there are no permanent bonds in the sample; for example, if $P=0.6$, then, 60% of the nanoparticles are connected by a permanent bond. (Note that the latter permanent bonds are randomly distributed throughout the sample.) We examine the two cases of labile bond energy of $U_{0}^{(l)} = 33k_B T$ and $39k_B T$. We also consider the two cases of corona thickness of $q = 0.75$ and 1.25, and the two cases of stretching velocity of $v = 0.001$ and 0.005. As noted above, each link in the network corresponds to multiple reformable bonds, and may contain one permanent bond. The rates of rupture and formation of bonds within the links varies as a function of corona overlap and the nature of the bonds (labile/permanent). The links stretch due to an applied deformation with the maximum extent of the stretching corresponding to the contour length of the grafted chains. When the links are stretched, the force exerted on the bonds in the link increases with separation and facilitates bond rupture.

In the absence of an external force, the system exhibits a steady-state, where the rupture of labile bonds is balanced by bond formation, thus leading to the existence of a finite number of labile bonds in the overlap region between particles. Note that the model assumes that no bond formation is possible in the absence of overlap, so that $N_k = 0$ in the steady state at no overlap. The assumption concerning the absence of bond formation beyond the corona is equivalent to assuming an immediate retraction of arms upon bond rupture. Finally, we note that eq. (4) describes dynamics of the number of bonds in any situation, with or without the corona overlap.

3 Results and Discussion

An important aspect of our approach to modeling the mechanical behavior of the dual cross-linked networks is that we combine known features of the interaction between two PGNs [5,6] with the non-equilibrium kinetics of bond rupture and formation described by the Bell model [7]. Using this new approach, we analyze the materials’ mechanical performance by applying a tensile deformation to a sample at constant velocity (strain-controlled deformation), and determine the resulting force $F$ on the sample and the number of bonds per particle as functions of strain, $\varepsilon$.

The strain $\varepsilon$ is calculated as the ratio of the extension of the sample to the original length. The ductility of the sample is characterized by the strain at break, $\varepsilon_b$, which is determined as the strain at which the force required for deformation drops as the sample fractures. The work done by the external force to fracture the sample (work-to-break) is a measure of the toughness of the material. In the macroscopic, continuum limit, the toughness is calculated as the work-to-break per unit volume of the undeformed sample [10,11]. Because, however, our simulations are performed at the mesoscopic level, it is more appropriate to define toughness as
the work-to-break per one particle. Hence, the value of toughness, $W$, is determined by integrating the force-extension curve, and dividing the resulting work by the number of nanoparticles in the sample, $N_{PGN}$.

Here, each sample is composed of $N_{PGN} = 180$ particles, which are initially arranged in 12 rows, with 15 particles in each row (see Methodology). To quantify the properties of the material formed from the dual cross-linked PGNs, eight independent runs are performed at each set of specified model parameters, and then the Weibull statistics [12] is employed to determine the ductility and toughness.

### 3.1 Effects of the dual crosslinking on mechanical properties of PGNs

The behavior of the dual cross-linked PGNs depends on the strength of the labile bonds and the fraction of permanent bonds within the network. The energies of the labile bonds chosen here are such that for the weaker labile bonds ($U_{0}^{(l)} = 33k_B T$), the bond rupture rate is of the same order of magnitude as the tensile deformation strain rate, whereas for the stronger labile bonds ($U_{0}^{(l)} = 39k_B T$), the rupture rate is approximately two orders of magnitude lower than the strain rate. As described in the Methodology, for $0 < P \leq 1$, the inter-particle links encompass a single permanent bond in addition to the existing labile bonds. The energy of the permanent bond is taken to be $U_{0}^{(p)} = 45k_B T$, which corresponds to a bond rupture rate that is approximately five orders of magnitude lower than the strain rate. We first examine the material properties of dual cross-linked PGNs that have a corona thickness of $q = 0.75$ and are subjected to a strain-controlled tensile deformation applied at a constant velocity of $v = 0.001$ (corresponding to roughly 3.55 nm/s). Figure 2 presents the strain at break $\varepsilon_b$ (Fig 2a) and toughness $W$ (Fig 2b) of the samples, which contain the weaker (curves 1) and stronger (curves 2) labile bonds, as functions of the fraction of permanent bonds $P$. The data points and error bars shown in Fig 2 were obtained by averaging over eight independent simulation runs (see above).

As can be seen from Fig. 2, the presence of the permanent cross-links is crucial for optimal mechanical performance if the labile bonds are weak. At lower fractions of permanent bonds, the PGNs having the weaker labile bonds exhibit a very low toughness (see curve 1 in Fig 2b at $0 < P \leq 0.4$) and a strain at break of about 0.25 (see curve 1 in Fig 2a at $P < 0.2$). At higher values of $P$, the permanent bonds form an elastic skeleton in the latter system that leads to a notable improvement in the material properties. Namely, ductility of the system having the weaker labile bonds increases to $\varepsilon_b = 1.0$ at $P \geq 0.5$ (Fig 2a, curve 1), and toughness of the system exhibits an increase from $W \sim 1$ at $P = 0.5$ to $W \sim 3.5$ at $P = 1$ (Fig 2b, curve 1).

In contrast, the PGNs linked with the stronger labile bonds produce a ductile, tough material even in the absence of the permanent bonds, i.e., at $P = 0$ (see Figs 2a and 2b, curves 2). Introduction of permanent bonds into the system does not affect the strain at break, which remains at $\varepsilon_b = 1.0$ for $0 \leq P \leq 1$ as seen in Fig 2a, curve 2. The permanent bonds, however, improve the toughness of the material; namely, $W = 7$ at $P = 0$ is increased to $W = 11$ at $P = 1$ (Fig 2b, curve 2).

It is noteworthy that at $P = 1$, the toughness of the sample with the stronger labile bonds is three times greater than that of the sample with the weaker labile bonds (Fig 2b), whereas the strain at break is the same in the two systems (Fig 2a). This behavior, as well as the overall effect of dual cross-linking on the mechanical properties of PGNs, can be better understood as we analyze the materials’ tensile behavior in more detail in the following discussion.

Figures 3a and 3b show the force-strain curves for the samples having the weaker ($U_{0}^{(l)} = 33k_B T$) and stronger ($U_{0}^{(l)} = 39k_B T$) labile bonds at the fractions of permanent bonds of $P = 0, 0.6$, and 1. Each curve corresponds to a single run of the simulations for samples with a corona thickness of $q = 0.75$ and a tensile deformation that is applied at a constant velocity of $v = 0.001$. The arrows pointing downwards indicate sample breakage. Notably, the data in Fig. 2 on ductility and toughness were obtained by analyzing force-strain curves similar to those in Figs 3a and 3b.

Figures 3a and 3b indicate that the behavior of the dual cross-linked PGNs under tensile deformation is similar to that of ductile polymeric materials [10,11]. Namely, at the smaller strains, dual cross-linked PGNs behave as elastic materials. At a strain of about 15-20%, the samples reach a yield point, after which the force $F$ decreases (Figs 3a and 3b). (Recall that this force represents the resistance of the material to deformation.) After the yield point, the material exhibits two distinct behaviors, which depend quite markedly on $P$. Specifically, the force
can reach a local minimum and then increases before the breakage, as seen in Fig 3a at \( P = 0.6 \) and 1 and in Fig 3b at \( P = 1 \). The latter force-strain behavior is characteristic of polymeric materials that exhibit cold-drawing and necking [10,11]. Alternatively, the force can continue to decrease until the sample breaks, as seen in Fig. 3a at \( P = 0 \) and Fig. 3b at \( P = 0 \) and 0.6.

Figures 3a and 3b also reveal the significant effect that the energy of labile bonds has on the mechanical performance of dual cross-linked PGNs. The weaker labile bonds cannot withstand deformation without the presence of permanent bonds as the force \( F \) varies around some low value (see Fig 3a, \( P = 0 \)). The sample becomes elastic only after a sufficient amount of permanent bonds is added, so that at \( P = 1 \), the yield strain and force are about 15% and 10, respectively (Fig 3a). In contrast, at \( P = 0 \), the sample having the stronger labile bonds exhibits the yield point at 20% strain, and the force at yield is of \( F = 38 \) (Fig 3b). Introducing the permanent cross-links to the PGNs linked by the stronger labile bonds increases the yield force up to \( F = 50 \) at \( P = 1 \), and modifies the post-yield behavior so that the sample exhibits quite pronounced cold-drawing/necking at \( P = 1 \) (Fig 3b).

### 3.2 Effect of Corona thickness

The interaction forces between the cross-linked PGNs and the bond formation within the corona depend on the corona thickness, \( q \). At a constant grafting density (0.005 chains/nm\(^2\)), the value of \( q \) is controlled by the contour length of the grafted polymer chains, \( L \). Here, we examine how a variation in the corona thickness affects the response of the materials to a tensile deformation that is applied at a constant strain rate of \( v = 0.001 \) (3.55nm/s).

Figures 4 and 5 show comparison of the strain at break \( \varepsilon_b \) and toughness \( W \) for samples prepared from PGNs having a corona thickness of \( q = 0.75 \) (curves 1 in Fig 4 and 5) and 1.25 (curves 2 in Fig 4 and 5). At the given grafting density (see above), the latter values of \( q \) correspond to chain lengths of \( L = 8.88 \, r_0 \) and 16.3 \( r_0 \), respectively.

For the material with the weaker labile bonds, both the strain at break and the toughness of the sample increases with an increase in \( q \) at \( P > 0.6 \) (see Figs. 4a and 4b). Notably, at \( P = 1 \), the ductility is enhanced by approximately 40% and the toughness is increased by a factor of 1.8. For samples encompassing the stronger labile bonds (\( U_0^{(1)} = 39k_BT \)), the strain at break \( \varepsilon_b \) shows no statistically significant dependence on the corona thickness in the range \( 0 \leq P \leq 1 \) as seen in Fig. 5a. However, the PGNs having the thicker corona of \( q = 1.25 \) exhibit a greater toughness than those at \( q = 0.75 \) over the entire range of \( P \). It is seen in Fig. 5b that the toughness \( W \) increases by a factor of 1.6 with the increase in \( q \).

### 3.3 Effect of strain rate

The mechanical properties of elastomers are known to depend on the deformation rate owing to the viscoelastic relaxation of polymer chains. The dual cross-linked PGNs exhibit an additional, unique mechanism of relaxation, which is due to the rupture and formation of the labile bonds. Variations in the strain rate could alter the mechanical response of the system of labile bonds especially when the rate of rupture is force-dependent.

We examine how variations in the strain rate affect the behavior of the PGN samples, which encompass the weaker (\( U_0^{(1)} = 33k_BT \)) and stronger (\( U_0^{(1)} = 39k_BT \)) labile bonds at the fraction of permanent bonds \( 0 \leq P \leq 1 \) and the corona thickness of \( q = 0.75 \). For this purpose, the samples are subjected to the tensile deformation at the constant pulling velocities of \( v = 0.001 \) (3.55nm/s) and \( v = 0.005 \) (17.75nm/s). The results of computer simulations are summarized in Figure 6 and 7, which shows the strain at break \( \varepsilon_b \) and toughness \( W \) of the samples, and the labels "1" and "2" denote data obtained at the lower and higher velocity, respectively.

Figure 6 and 7 show that at the given parameters, the strain rate has no considerable effect on the ultimate tensile strains \( \varepsilon_b \) in the PGNs having the weaker (Fig. 6a) and stronger (Fig. 7a) labile bonds. However, an increase in the strain rate results in an increase in the toughness \( W \) of the samples, and the observed enhancement of toughness depends on the strength of labile bonds (Figs. 6b and 7b).

For the samples having the weaker labile bonds, there is no statistically significant effect of the pulling velocity on \( W \) at \( P < 0.6 \), and ~40% increase in \( W \) is observed at \( P = 1 \) (Fig. 6b). In contrast, the material encompassing the stronger labile bonds exhibits ~70% increase in \( W \) at the higher strain rate even when no permanent bonds are
present \( (P = 0) \), and the enhancement of toughness is about 80% at \( P = 1 \) (Fig. 7b).

4 Conclusions

We find that the mechanical behavior of the network can be tailored by altering the bond energies of the labile bonds, the fraction of permanent bonds in the network and the thickness of the polymer corona. In particular, for a network with weaker labile bonds, an increase in fraction of permanent bonds and the contour length of the chain can yield a tough network that behaves like a polymeric material, which exhibits cold drawing/necking. On the other hand, similar changes to the network with stronger labile bonds lead to an increase in toughness, with the network characteristics being similar to that of a purely ductile material. Variations in the ratio between the strain rate and the bond rupture rate are also found to affect the response of the networks. Our model provides a powerful approach for predicting how critical features of the system affect the performance of cross-linked polymer-grafted nanoparticles.

References


Figures

Fig. 1. Components in the multi-scale model
Fig. 2. Effect of fraction of permanent bonds, $P$, and labile bond energy, $U_0^{(l)}/k_B T$, (red and blue lines denote $U_0^{(l)}/k_B T = 33$ and 39, respectively). (a) Strain at break, $\varepsilon_b$, as a function of fraction of permanent bonds, $P$. (b) Toughness, $W$, as a function of fraction of permanent bonds, $P$.

Fig. 3. Effect of fraction of permanent bonds, $P$, on mechanical response of network. (a) Force($F$)-strain($\varepsilon$) curves at $P=0$, 0.6 and 1 (black, green and red curves, respectively) for $U_0^{(l)}/k_B T = 33$. (b) Force($F$)-strain($\varepsilon$) curves at $P=0$, 0.6 and 1 for $U_0^{(l)}/k_B T = 39$. 
Fig. 4. Effect of fraction of permanent bonds, $P$, and corona thickness, $q$ (blue and green lines denote $q=0.75$ and 1.25 samples, respectively) (a) Strain at break, $\varepsilon_b$, as a function of fraction of permanent bonds, $P$. (b) Toughness, $W$, as a function of fraction of permanent bonds, $P$, for $U_0^{(i)}/k_BT = 33$.

Fig. 5. Effect of fraction of permanent bonds, $P$, and corona thickness, $q$ (blue and green lines denote $q=0.75$ and 1.25 samples, respectively) (a) Strain at break, $\varepsilon_b$, as a function of fraction of permanent bonds, $P$. (b) Toughness, $W$, as a function of fraction of permanent bonds, $P$, for $U_0^{(i)}/k_BT = 39$. 
Fig. 6. Effect of fraction of permanent bonds, $P$, and pulling velocity (blue and red lines denote pulling velocities $v=0.001$ and 0.005, respectively). 
(a) Strain at break, $\varepsilon_b$, as a function of fraction of permanent bonds, $P$. 
(b) Toughness, $W$, as a function of fraction of permanent bonds, $P$, for $U_0^{(i)}/k_BT = 33$.

Fig. 7. Effect of fraction of permanent bonds, $P$, and pulling velocity (blue and red lines denote pulling velocities $v=0.001$ and 0.005, respectively). 
(a) Strain at break, $\varepsilon_b$, as a function of fraction of permanent bonds, $P$. 
(b) Toughness, $W$, as a function of fraction of permanent bonds, $P$, for $U_0^{(i)}/k_BT = 39$. 