

Molecular Mechanisms of Failure in Polymer Nanocomposites

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Molecular dynamics simulations of polymers reinforced with nanoscopic filler particles reveal the mechanisms by which nanofillers improve the toughness of the material. We find that the mobility of the nanofiller particle, rather than its surface area, controls its ability to dissipate energy. Our results show similarities between the toughening mechanisms observed in polymer nanocomposites and those postulated for biological structural materials such as spider silk and abalone adhesive.

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The practice of adding micron sized inorganic filler particles to reinforce polymeric materials can be traced back to the early years of the composite industry. The design of such conventional composites has been focused on maximizing the interaction between the polymer matrix and the filler [1]. This is commonly achieved by using smaller filler particles to increase the surface area available for interaction with the matrix. With the emergence of synthetic methods that can produce nanometer sized fillers [2,3], resulting in an enormous increase of surface area, polymers reinforced with nanoscale particles should show vastly improved properties. Yet, experimental evidence suggests that a simple extrapolation of the design paradigms of conventional composites cannot be used to predict the behavior of nanocomposites [4–6]. The origin of these differences between conventional and nanocomposites, however, is still not known.

In this Letter, we use a molecular dynamics simulation to analyze the molecular mechanisms by which nanosized filler particles reinforce polymeric matrices. We find that the ability of the nanofiller to increase the toughness of the material results from the equivalence of time scales of motion for the polymer and the filler. We show that the mobility of the nanofiller, rather than its surface area, is key to the performance of the nanocomposite and that this mobility is a complex function of the size of the filler, the attraction between the polymer and the filler, and the thermodynamic state of the matrix. Our results show striking similarities between the toughening mechanisms in polymer nanocomposites and those postulated for naturally occurring biological materials which also contain nano-scaled assemblies, such as spider silk [7] and abalone adhesive [8].

Experimental studies have shown that, while the addition of nanoparticles results in a large increase in the yield stress and the energy to break for polymeric materials that are above the glass transition temperature (T_g) [4,5], only very modest reinforcement is observed for polymeric materials that are below T_g [6]. These results appear to contradict existing molecular models of reinforcement of polymer matrices by conventional fillers, which assume that the reinforcing properties of the filler result only from

the stiffening of the polymer matrix due to the attraction between the filler and the polymer [9–13]. As a result, these models imply that the ability of the filler to toughen the matrix should not depend on the thermodynamic state of the polymeric material. Further, while these theories predict that the reinforcing effects should only be manifested when filler loadings are close to the percolation threshold of the system (where the stiffening mechanism can dominate the properties of the material), in polymer nanocomposites considerable reinforcement is observed even for small concentrations of nanofillers [4–6].

To resolve these open issues, we studied the mechanisms of failure in polymer nanocomposites by using a molecular dynamics (MD) simulation. In the simulation, we modeled the polymer as a linear polymer chain with $N = 64$ segments. Monomers of mass m separated by a distance r , interact via a generalized Lennard-Jones (LJ) [14] potential of the form $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ for $r < r^c = 2.5\sigma$. Here ϵ and σ are the characteristic energy and length scales, and the potential is zero for $r > r^c$. Adjacent monomers along the chain are coupled by an additional potential that prevents chain breaking [15]. The filler particle is modeled as a sphere, with a length scale denoted by σ_f . The interaction between the polymer and the filler is mediated by another LJ potential of the form $V(r) = 4\epsilon_{fp}\{[\sigma/(r-s)]^{12} - [\sigma/(r-s)]^6\}$, where ϵ_{fp} is the interaction between the filler and the polymer and $s = (\sigma_f - \sigma)/2$ [16]. It is important to note that though the filler particles used in the simulation are small, the relevant length scale here is the radius of the filler particle compared with the radius of gyration of the chain. Using these scaled units, in our simulation the largest filler size we use is 0.6 times the radius of gyration of the chain, a ratio that is comparable to experimental systems such as the ones in [5]. We set the density of the filler = 3ρ , where ρ is the density of the monomer. The system used contained 4096 particles (monomers + fillers). Periodic boundary conditions were applied in the x and y directions, while the z direction was bounded by walls. The lattice sites of each wall formed two (111) layers of an fcc crystal. Temperature control was maintained by damping the wall atoms by a Langevin factor. The chain lengths used in the

simulation are slightly below the entanglement length of the polymer chain [17], but, by normalizing the work to failure by the work to failure in the absence of any filler particles, we are able to isolate the role of the filler in the reinforcement of the matrix and we anticipate that our results will also hold for longer chain lengths.

The system was equilibrated and care was taken to ensure that the filler was uniformly distributed in the matrix and that there were no residual stresses present in the material. To simulate the fracture of the nanocomposite, the top wall was moved at velocities ranging from $v = 0.03 - 0.24\sigma/\tau$. The interaction between the polymer and the wall was chosen such that when the walls were moved apart, failure would occur only in the interior of the composite and not at the wall/composite interface [16,17]. The pulling rates that were used in the simulation are similar to ones that have been used in recent literature [18–21] and have been shown to recover the correct physical behavior for polymeric materials [22]. We studied the system at temperatures of $T = 1.1$ and $0.3\epsilon/(kT)$. The glass transition temperature of the system has been estimated to be between $T = 0.5-0.6\epsilon/(kT)$ [18]. Runs for temperatures above T_g were averaged over three independent equilibrium conformations of the system. Runs below T_g showed more variation and were averaged using between 5–10 independent equilibrium starting conformations.

An examination of the force-distance curves for materials (Fig. 1) with and without the nanofiller reveals possible clues about the mechanisms by which the nanofiller toughens the composite. The maximum in the force-distance curves corresponds to the onset of cavitation in the material. With the addition of nanofiller, the attraction between the filler and the polymer increases the yield stress for cavitation (and, consequently, its modulus), and this effect occurs for both rubbery and glassy polymer matrices. This mechanism is similar to the stiffening effect of conventional filled composites, where the yield stress for cavitation also increases with an increase in the attraction

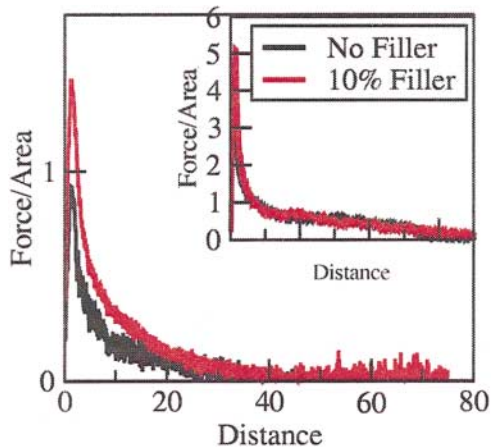


FIG. 1 (color). Force distance curves with and without the nanofillers. In these curves, the fillers have $\sigma_f = 3\sigma$, $\epsilon_{fp} = 4\epsilon$, and $v = 0.03\sigma/\tau$. The main curve is at a temperature of $T = 1.1\epsilon/kT$ and the inset is for $T = 0.3\epsilon/kT$.

between the filler and the polymer. What is unusual about the nanofiller, though, is that for rubbery polymer matrices, after cavitation has occurred the nanofillers continue to actively resist the growth of the cavity. This can be seen as the force-distance curve for the polymer nanocomposite is always higher than the case when there is no filler present. This represents a significant departure from conventional filled composites where after failure occurs, as the fillers are large and therefore essentially static, their role is simply to passively act as a barrier to crack propagation. The ability of the nanofiller to resist cavity growth, however, disappears when the polymer matrix is below T_g (Fig. 1, inset). Since the contribution to the total work is largely controlled by the behavior of the material after the cavity is formed (the long tail accounts for 80–90% of the total work to failure for both above and below T_g), to determine the factors that control the toughness of the nanocomposite we have to understand the processes that occur during the growth of the cavity.

To isolate the role of the filler on the properties of the system after cavitation has occurred, in Fig. 2 we plot the work to failure after cavitation normalized by the work to failure when no filler is present, as a function of the size of the filler particle. This plot seems to indicate that the deformation processes occurring in the nanocomposite are in agreement with the general design principles of conventional composites, i.e., an increase in surface area (which results from using smaller filler particles) and an increase in the attraction between the filler and the polymer (increasing ϵ_{fp}), improves the toughness of the nanocomposite. Yet, the large enhancement of toughness for rubbery polymers occurs at a filler loading of 10%, which

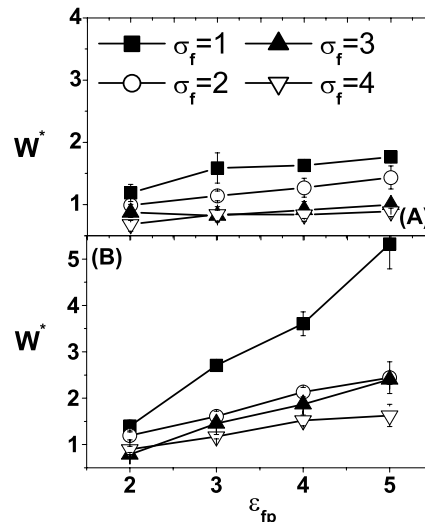


FIG. 2. The normalized work to failure, W^* , as a function of the size of the filler particle, σ_f . In all cases shown here the pulling velocity was $v = 0.03\sigma/\tau$. (a) The temperature was fixed at $T = 0.3\epsilon/kT$. (b) The temperature was fixed at $T = 1.1\epsilon/kT$. W^* is defined as the work to failure of the nanocomposite after cavitation has occurred divided by the work to failure after cavitation when no filler is present in the system. Similar trends were observed for the other pulling velocities.

is far less than what is used in conventional materials. Also, in agreement with experimental findings [6], we find little to no improvement in the toughness of glassy polymeric materials. The ability of the nanofiller to toughen the material thus appears to be a function of the thermodynamic state of the matrix.

The effect of the state of the matrix on the ability of nanofiller to resist cavity growth, can be determined by calculating the filler-filler correlation function, $g(r)$, during the deformation process. $g(r) = n(r)/\sum n(r)$, where $n(r)$ is the number of fillers that are located at a distance r from a given filler, and, $g(r)$ is normalized by the total number of filler pairs in the system. Two points should be noted from Fig. 3. First, the presence of two peaks in $g(r)$ is a result of failure taking place through cavitation. The second peak occurs since there is a depletion of filler in the region where the cavity is formed [see Figs. 4(a) and 4(b)]. Second, the amount of filler that is present in the material that bridges the cavity is a measure of its ability to resist the growth of the cavity, as the more filler that is present, the more the force necessary to grow the cavity. The effect of the thermodynamic state of the matrix can then be seen in Fig. 3. As the deformation proceeds, the matrix that is above T_g always shows a larger amount of filler present in the bridge region, than when the polymer matrix is below its T_g . This can also be clearly seen in the MD snapshots [Figs. 4(a) and 4(b)] which show that there is much more filler present in the region around the cavity for rubbery polymer matrices [23]. The ability of the nanofiller to improve the mechanical properties of the polymer matrix thus goes beyond the simple stiffening argument used in conventional composites.

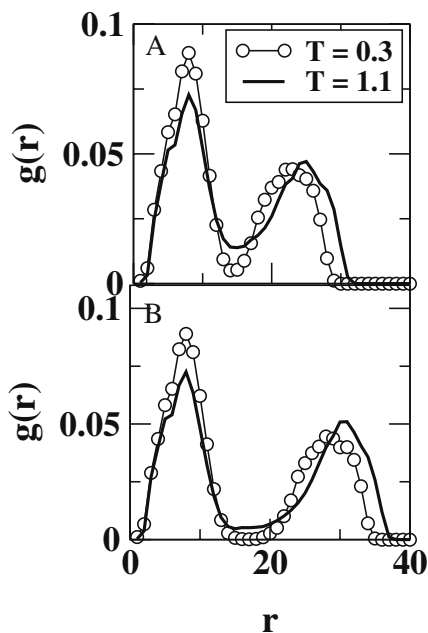


FIG. 3. Time evolution of the filler-filler correlation function, $g(r)$, for two different temperatures, at (a) time = 700τ and (b) 900τ .

In order to hypothesize a mechanism by which nanofillers toughen the polymer, one can draw an analogy between polymer nanocomposites and biological structural materials that also have assemblies in the nanometer scale range, such as spider silk or abalone adhesive. In spider silk they take the form of nanocrystallites [7], while in abalone adhesive the key components appear to be protein assemblies [8]. The unusual toughness of these biological materials has been postulated to be a result of the ability of the nanoscaled assemblies to actively participate in the mechanisms of energy dissipation. The key point that allows us to make the analogy between nanocomposites and these naturally occurring materials is that in all these systems, the nanostructure participates in the energy dissipation process during the entire deformation process. In biological materials this participation has been postulated to take the form of an additional dissipation through either the unbinding of protein assemblies (abalone adhesive), or of the nanocrystallites (spider silk). However, since the nanofiller cannot deform, the source of the additional dissipation has to be a result of some other mechanism.

We believe that this additional dissipative mechanism is a result of the mobility of the nanofiller particle. Since the filler is of the same size as the polymer chain, the time scales for motion for the filler and the polymer are comparable. As a result, during the deformation process the filler can create temporary cross links between the polymer chains, thereby creating a local region of enhanced strength and consequently retarding the growth of the cavity. Since the mobility of the filler particle is severely reduced when the polymer matrix is below T_g , the ability of the nanofiller to dissipate energy is also reduced, resulting in almost no improvement in the toughness of the material. Above T_g , the nanofiller is mobile enough to form the temporary bonds that allow it to dissipate energy and thus rubbery matrices benefit the most from the addition of nanofillers. The mobility of the nanofiller, however, is determined by both the size of the filler particle and the interaction between the filler and the polymer. Smaller filler particles are more mobile, but as the interaction between the filler and the polymer is increased one would expect the differences between fillers of different sizes to reduce, as in this

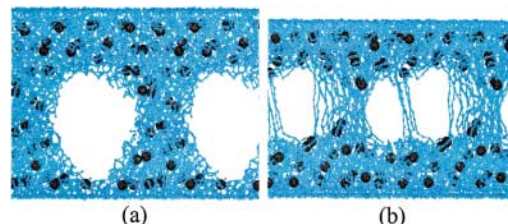


FIG. 4 (color). MD snapshots of the system. (a) At a temperature of $T = 1.1$ and (b) at a temperature of $T = 0.3$. The size of the simulation box in the z direction is smaller at the lower temperature of $T = 0.3$ due to the densification that occurs below T_g . Both snapshots correspond to $\sigma_f = 3\sigma$, $\epsilon_{fp} = 4\epsilon$, and $\nu = 0.03\sigma/\tau$ and are taken at a time = 500τ . The filler particles are colored in black.

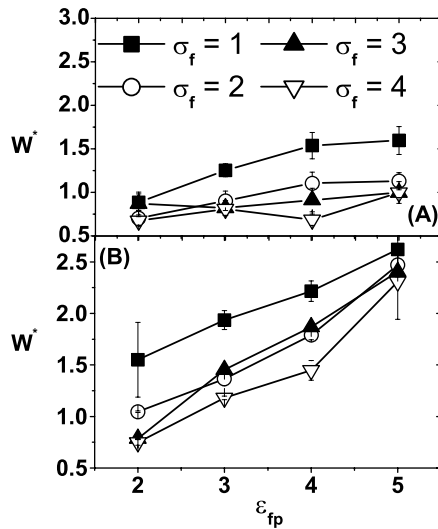


FIG. 5. Normalized work to failure, W^* for filler particles of different sizes but with the same surface area. (a) The temperature was fixed at $T = 0.3$. (b) The temperature was fixed at $T = 1.1$. For both curves $v = 0.03(\sigma/\tau)$.

limit, the fillers are constrained to move along with the polymer matrix.

This hypothesis, that the mobility of the nanofiller is key to the performance of the nanocomposite, can be confirmed by running a set of simulations in which the surface area of the fillers is kept fixed while the other parameters, such as the size of the filler, temperature and the filler-polymer attraction are varied. By our analysis, for nanoscaled fillers in a polymer matrix that is above its T_g , the more mobile fillers (relative to the matrix) should always be better at toughening the polymer nanocomposite. Indeed, as can be seen from Fig. 5, at constant surface area, the smaller filler particles are always better at toughening the nanocomposite. The interplay between the mobility of the filler, its size, and the filler polymer interaction can also be seen, as when we increase ϵ_{fp} , we find that the curves for the different filler sizes start to coincide until finally at high enough filler-polymer attraction all filler sizes result in the same strength. When the polymer matrix is below T_g , little to no effect is seen, as all filler particles (except the smallest) result in the same strengthening effect.

Our analysis of the processes that control the behavior of polymer nanocomposites indicate that the equivalence of time scales of motion of the filler and the polymer results in the enhanced toughness that is seen over conventional composite materials. The role of the nanofiller is thus not limited to its ability to stiffen the material, rather the key seems to be its ability to dissipate energy even after failure has occurred. The broader implications of this analysis suggest that even in biological structural materials (which have built-in energy dissipation methods), an additional factor that has to be considered is the mobility of these assemblies.

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- [22] The ratio of the pulling rate to the diffusion constant is on the order of 10^2 when the matrix is above its T_g . This translates into a Peclet number under shear (using a similar wall velocity) of between 100–3000 for the entire range of filler sizes and filler-polymer interaction, which is comparable with experimental Peclet numbers [see, e.g., R. G. Larson, *The Structure and Rheology of Complex Fluids* (Oxford University Press, New York, 1999)]. The pulling rates used below T_g are comparable to the ones in Refs. [20,21].
- [23] In the MD snapshots only a single cavity is observed in most cases. We believe that this a result of the system size that we use since multiple cavities are observed for larger systems such as in [20]. It should be noted, however, that the work to failure is not a function of the system size at the chain lengths and parameters that we use, since our results (in the absence of fillers) give the same value for the work to failure when compared with system sizes that are at least 5–10 times larger [20].