Influence of Nanoparticle Additives on the Fragility of Polymer Glass Formation and the Buchenau Relation

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We investigate the impact of the addition of nanoparticles (NP) on the fragility of a model glass-forming polymer melt by molecular dynamics simulations. We find significant changes in fragility for nanoparticle volume fractions $\phi$ exceeding $\approx 5\%$, where fragility changes correlate with the inverse variance of the magnitude of the Debye-Waller factor $\langle u^2 \rangle$, a measure of local “stiffness” fluctuations. We also confirm the validity of the Buchenau relationship between $\langle u^2 \rangle$ and the structural relaxation time $\tau$ for all $\phi$ and polymer-NP interaction types.

The addition of a small concentration of nanoparticles (NP) to glass-forming polymer materials can lead to large property changes that are difficult to comprehend by extension of the effects of macroscopic filler additives and the corresponding theory of composite materials [1, 2]. For well-dispersed NP, these changes are often rationalized by the large surface-to-volume ratio of these particles, which results in a greater interfacial interaction with the surrounding polymer matrix. However, this is not a unique mechanism for all property changes, and other mechanisms, such as chain bridging [3, 4, 5] and NP self-assembly into extended structures [6], are under current discussion.

Of the many affected properties, changes in the glass transition temperature $T_g$ have been particularly emphasized, since changes in $T_g$ are correlated with changes in diverse transport phenomena. Specifically, both experimental and theoretical studies have indicated a tendency for highly attractive or repulsive (non-attractive) polymer-NP interactions to increase or decrease $T_g$, respectively. This phenomenon has been rationalized in terms of the influence of the NP boundary interactions on the dynamics of polymers within an interfacial layer near the NP surfaces [7, 8, 9, 10]. In particular, the interfacial polymer layer around the NP shows a slowing down (increased $T_g$) or acceleration of dynamics (decreased $T_g$) when the polymer-NP interactions are attractive or repulsive, respectively. These observations led to the suggestion that the interparticle distance (related to the particle concentration for uniformly distributed NP) plays a role analogous to film thickness in thin polymer films [7, 9].

Changes of $T_g$, while informative, provide only a limited understanding of how NP affect the properties of glass-forming polymer melts. It is also natural to expect that the temperature dependence of the dynamic properties approaching $T_g$, referred to as the “fragility” of glass formation [11, 12], will be altered. Fragility changes have been argued for on theoretical grounds [12], based on the finding that any factor that influences the molecular packing in the glass state ($T < T_g$) should also alter the fragility of glass formation. The NP we study should be particularly effective at modifying molecular packing, since their size is roughly commensurate with the heterogeneity scale of fluids near their $T_g$ (i.e., $2$ nm to $3$ nm) [13].

The present work addresses how polymer-NP interactions and NP concentration affect the fragility of glass formation, and how fragility changes relate to variations in the high frequency molecular dynamics, as measured by the Debye-Waller factor $\langle u^2 \rangle$. We find that the addition of nanoparticles can increase or decrease fragility, depending on the polymer-NP interaction, and that this effect becomes more pronounced with increasing $\phi$. We relate these changes to fluctuations of $\langle u^2 \rangle$, which can be interpreted as a change in the fluctuations of the local molecular stiffness [14]. We also find that the Buchenau relation [15] holds with remarkable generality for all $\phi$ and interaction types, confirming the relationship between high frequency relaxation and structural relaxation under rather general circumstances.

Our findings are based on equilibrium molecular dynamics simulations of a nanoparticle surrounded by a dense polymer melt, as well as simulations of a pure melt for comparison purposes. We utilize periodic boundary conditions so that our results correspond to a uniform dispersion of NP. The polymers are modeled by a well-studied bead-spring model [16]. All monomer pairs interact via a Lennard-Jones (LJ) potential $V_{LJ}$, and bonded monomers along a chain are connected via a FENE anharmonic spring potential. The NP consists of 356 Lennard-Jones particles bonded to form an icosahedral NP; the facet size of the NP roughly equals the equilibrium end-to-end distance for a chain of 20 monomers. Details of the simulation protocol and our model potentials can be found in ref. [9]; further studies of the clustering and mechanical properties related to this model are presented in [17, 18].

We simulate systems with 100, 200, or 400 chains of $M = 20$ monomers each (for totals of $N = 2000$, 4000, and 8000 monomers) to address the effect of varying the NP volume fraction. Under constant pressure conditions,
the addition of nanoparticles can give rise to a change in the overall melt density. A slight change in density can cause a significant but trivial change in the dynamic properties relative to the pure melt. In order to probe only changes caused by the interactions between the NP and the polymer melt, we have matched the density of monomers far from the NP with that of the pure polymer melt.

To quantify changes in $T_g$ and fragility, we evaluate effect of $\phi$ and the polymer-NP interactions on $\tau$, measured from the decay of the coherent intermediate scattering function (see supplementary information for a technical description). The effects of these interactions on $\tau$ for some $\phi$ were already presented in ref. [9]; here we provide additional simulation data and expand the analysis considered before to include the effect of the NP on fragility. As expected, Fig. 1 shows that attractive polymer-NP interactions slow the relaxation ($\tau$ becomes larger), while non-attractive polymer-NP interactions give rise to an increased rate of relaxation ($\tau$ becomes smaller). The effect of $\phi$ is more clearly seen by rescaling $\tau$ by $\tau_{\text{pure}}$ of the pure melt, which shows that $\tau$ can be altered by a factor of more than an order of magnitude due to the NP. The effect of the NP is more pronounced at low $T$, since at high $T$ the polymer-NP interaction potential strength is weak in comparison with the system kinetic energy.

We next examine how these changes in $\tau$ affect $T_g$ and fragility. The inset of Fig. 2 confirms that $T_g$ increases when there is attraction, and decreases with non-attractive interactions. To estimate $T_g$, we fit the data using the Vogel-Fulcher-Tammann (VFT) expression [11]

$$\tau = \tau_0 e^{D/(T/T_0 - 1)}.$$  \hspace{1cm} (1)

$T_0$ is an extrapolated divergence temperature of $\tau$, while $D$ provides a measure of the fragility. We use the VFT fit to estimate $T_g$ based on the condition that $\tau(T_g) = 100$ s (the canonical definition of the laboratory glass transition [11]), assuming the one time unit in standard LJ reduced units corresponds to 1 ps (reduced units are defined in the supplementary information).

Since $T_g$ changes have been the focus of previous work, we emphasize how polymer-NP interactions and $\phi$ affect fragility. Since there is no single agreed upon measure of fragility, we consider several different measures. First, as indicated above, the parameter $D$ from a VFT fit to $\tau$ is widely utilized; specifically, a larger value of $D$ indicates a stronger (less fragile) glass-forming fluid so that $1/D$ increases with increasing fragility. Another common estimate of the fragility is defined by the temperature ratios $T_0/T_g$ or $T_g/T_c$. We estimate $T_c$ using the power-law form $\tau \sim (T/T_c - 1)^{-\gamma}$ in an appropriate temperature range (see supplementary information for fitting details). Since strong systems should have relatively weak temperature dependence of $\tau$ approaching $T_g$, larger values of $T_0/T_g$ or $T_g/T_c$ correspond to more fragile systems. Finally, we use the VFT fit to estimate the fragility from the $T$ dependence of $\tau$ near $T_g$ using the most commonly advocated fragility definition [19].

$$m = d(\ln \tau)/d(T_g/T)|_{T_g},$$ \hspace{1cm} (2)

For strong systems, the rate of change of $\tau$ with respect
to $T$ is smaller than that of fragile systems; hence $m$ is larger for more fragile glass-forming fluids. We must rely on an extrapolation of the VFT fit to determine $m$, so that caution should be exercised interpreting the precise values of our $m$ estimates.

We summarize the results for the various fragility metrics in Fig. 2 where we find that attractive polymer-NP interactions lead to more fragile glass formation as a function of $\phi$; conversely, non-attractive polymer-NP interactions lead to stronger glass formation. These changes are non-trivial, since $T_g$ is independent or anticorrelated with fragility in some systems [20]. Our findings for the changes of fragility are consistent with several experimental studies. Bansal et al. [7] found that dispersions of NP having repulsive interactions caused $T_g$ to decrease, accompanied by an appreciable broadening of the glass transition region. Though they did not interpret their results in terms of fragility, the increased breadth is indicative of increased strength (decreased fragility), as we observe. For the case of fullerenes dispersed in polystyrene, Sauz et al. [21] reported behavior expected for attractive polymer-NP interactions, namely an increase in $T_g$, accompanied by an increased fragility. Other studies have indicated no detectable or only a small change in the fragility with NP additive for small $\phi$ [22]. The apparent absence of fragility changes at small $\phi$ is also consistent with our results, which likewise show nearly undetectable changes in this concentration range.

Having established the variation in $T_g$ and fragility for the various systems, we now examine how these changes can be understood from the high frequency melt dynamics. Both experiments and simulations have shown that the Debye-Waller factor $\langle u^2 \rangle$ can be related to the low frequency relaxation associated with large scale structural relaxation [23] [24]. $\langle u^2 \rangle$ measures monomer displacement on a time scale over which the particles are caged by their neighbors, and is accessible from both x-ray and neutron scattering measurements [24]. Since $\langle u^2 \rangle$ is usually determined experimentally at a fixed instrumental time corresponding to the time scale on the order of vibrational motion of the molecules, we determine the mean-squared chain segment displacement (MSD) at a vibrational time scale, specifically at a reduced time equal to 1.53, $\approx$ the mean collision time.

Fig. 3 shows that, when normalized by the behavior of the pure melt, the changes in $\langle u^2 \rangle_{\text{pure}}/\langle u^2 \rangle$ are very similar to those observed for $\log(\tau/\tau_{\text{pure}})$. Evidently, the $\langle u^2 \rangle$ is sensitive not only to changes in $\phi$, but also to the polymer-NP interactions. This affirms that $\langle u^2 \rangle$ is a potentially useful indicator of changes in low frequency relaxation.

To understand how the changes in fragility relate to the high frequency dynamics, we must look beyond changes in $\langle u^2 \rangle$. It has been argued [12] [26] that the changes in fragility can be connected with the efficiency of local packing, which is accompanied by changes in the fluctuations in the local moduli. Since the inverse of $\langle u^2 \rangle$ is a measure of the local liquid rigidity at high frequency [14], we expect that fragility changes should be reflected in the variance $\sigma^2 = \langle u^4 \rangle - \langle u^2 \rangle^2$ of the Debye-Waller factor.

Figure 4 shows that, when normalized by the value for the pure melt, $\sigma$ is larger for stronger glass formation (the non-attractive interactions), and smaller in the more fragile case (attractive interactions) in the $T$ range considered. If we consider the normalized inverse of this quantity $\sigma_{\text{pure}}/\sigma$, we can examine to the relative variance in the local stiffness. These results show that the stronger systems have relatively smaller fluctuations in the local
stiffness, while the more fragile systems have relatively larger fluctuations. This is consistent with the idea that the stronger systems should be better packed, and vice-versa for the more fragile systems. Hence, $1/\sigma$ appears to be reflective of a change in fragility.

Finally, we explore the proposed quantitative relation between $\tau$ and $\langle u^2 \rangle$ provided by the “Buchenau relation,”

$$\tau = \tau_B u_0^2 / \langle u^2 \rangle,$$

where $\tau_B$ and $u_0^2$ are system dependent constants. This relation has been verified for a number of systems, including the pure polymer melt currently under investigation [21]. Larini et al. [22] have shown that a generalization of this relation seems to hold for diverse collection of simulated and real fluids over a wide range of temperatures, suggesting an amazing generality of the Buchenau expression, supporting the proposal that $\tau$ is a universal function of $\langle u^2 \rangle$. The inset in Fig. 5 shows a striking agreement of our relaxation data with the Buchenau relation, the correlation becoming better at lower $T$. Deviations at high $T$ can be expected since $\langle u^2 \rangle$ becomes progressively ill-defined as $T$ increases. More significantly, if we reduce $\tau$ and $\langle u^2 \rangle$ by the corresponding fit parameters $\tau_B$ and $u_0^2$, we find that the data for all $\phi$ and $T$ can all be collapsed to a single master curve (main part of figure). This reinforces the somewhat surprising fact that the slow dynamics of the system are intimately connected with the high frequency vibrational properties of the system, as epitomized by $\langle u^2 \rangle$.

Similar to our findings, Riggleman et al. [23] have suggested a link between fragility variations and elastic constant (shear modulus) fluctuations in polymer nanocomposites in the glass state, but this was not verified through a direct determination of fragility.

Care must be taken in comparing the glass below $T_g$ with a liquid approaching $T_g$ from above, as recent results suggest opposite trends may result. For example, Riggleman et al. [23] show that a decrease of the fragility actually results in a stiffening below $T_g$, but a softening above $T_g$, consistent with our results above $T_g$. Such an inversion between relative material stiffness and relaxation times near $T_g$ has been suggested to be a general phenomenon [24], having potential applications in relation to scratch resistance of films, stabilizing nano-fabricated structures formed by lithography and nano-imprint technology, and the preservation of drugs in glass-forming preservative formulations [25].

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