ACSNANO

Article

Subscriber access provided by University of Florida | Smathers Libraries

University of Florida

Big Effect of Small Nanoparticles: A Shift in Paradigm for Polymer Nanocomposites

Shiwang Cheng, Shi-Jie Xie, Jan-Michael Y. Carrillo, Bobby Carroll, Halie Martin, Peng-Fei Cao, Mark D. Dadmun, Bobby G. Sumpter, Vladimir N Novikov, Kenneth S. Schweizer, and Alexei P. Sokolov ACS Nano, Just Accepted Manuscript • DOI: 10.1021/acsnano.6b07172 • Publication Date (Web): 04 Jan 2017 Downloaded from http://pubs.acs.org on January 5, 2017

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Nano is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Big Effect of Small Nanoparticles: A Shift in Paradigm for Polymer

Nanocomposites

Shiwang Cheng^{1*}, Shi-Jie Xie², Jan-Michael Y. Carrillo^{3,4}, Bobby Carroll⁵, Halie Martin⁶, Peng-Fei Cao¹, Mark D. Dadmun^{1,6}, Bobby G. Sumpter^{3,4}, Vladimir N.

Novikov⁶, Kenneth S. Schweizer² and Alexei P. Sokolov^{1,5,6*}

¹Chemical Sciences Division, Oak Ridge National Laboratory,

Oak Ridge, Tennessee 37831, United States

²Departments of Materials Science and Chemistry, Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801, United States

³Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

⁴Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

⁵Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, United States

⁶Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States

Abstract

Polymer nanocomposites (PNCs) are important materials that are widely used in many current technologies and potentially have broader applications in the future due to their excellent property tunability, light weight and low cost. However, expanding the limits in property enhancement remains a fundamental scientific challenge. Here, we demonstrate that well-dispersed, small (diameter ~1.8 nm) nanoparticles with attractive interactions lead to unexpectedly large and qualitatively different changes in PNC structural dynamics in comparison to conventional nanocomposites based on particles of diameter ~10-50 nm. At the same time, the zero-shear viscosity at high temperatures remains comparable to that of the neat polymer, thereby retaining good processibility and resolving a major challenge in PNC applications. Our results suggest that the nanoparticle mobility and relatively short lifetimes of nanoparticle-polymer associations open qualitatively different horizons in tunability of macroscopic properties in nanocomposites with high potential for the development of advanced functional materials.

Keywords: polymer nanocomposites, small nanoparticles, glass transition, fragility, apparent disentanglement

^{*} Corresponding authors.

Email address: S.C: chengs@ornl.gov; A.P. S:sokolov@utk.edu;

The addition of nanoparticles to dense polymer matrices results in polymer nanocomposites (PNCs) with significantly altered segmental and chain relaxation,¹⁻³ leading to a wide tunability in macroscopic properties,⁴⁻⁶ including the glass transition¹⁻² and viscoelastic response.³ An interfacial polymer layer of 1-5 nanometers thick surrounding nanoparticles (NPs) is well established.⁷⁻¹³ and has been regarded as the main mechanism of modifying macroscopic properties of PNCs.¹⁴⁻¹⁸ Decreasing NP size increases the interfacial layer volume fraction at fixed loading,¹⁵ and could enhance desirable changes. However, one expects that there is an optimum NP size since small enough particles typically plasticize the polymer matrix,¹⁹⁻²¹ thereby speeding up dynamics, decreasing T_g, and reversing desirable thermomechanical property changes.²² Moreover, weak interactions between polymer and nanoparticles typically lead to aggregation and poor dispersion that often complicate studies of PNCs with small nanoparticles, resulting in nonequilibrium effects and loss of interfacial area at high loadings.²² As a result, only a few publications have analyzed the influence of small (diameter D~1-2 nm) welldispersed nanoparticles on PNC properties, although some revealed relatively large effects at low loadings (~1-2 vol%).²³⁻²⁴

Here we present a detailed study of PNCs with well-dispersed, small (of order the polymer segment) attractive nanoparticles. We discover unexpectedly large and qualitatively different dynamical effects relative to conventional PNCs with D~10-50 nm nanoparticles. Combining experiment, theory and simulations, we provide an understanding of these effects, which suggests a promising strategy for tuning

ACS Nano

macroscopic PNC properties over a considerably broader range than was previously possible.

RESULTS

We blend Poly(2-vinylpyridine) (P2VP) ($M_w = 101 \text{ kg/mol}$) with octaaminophenyl polyhedral oligomeric silsesquioxane (OAPS, Fig.1b) nanoparticles of diameter D = 1.8 nm, nearly identical to the polymer Kuhn segment size, $l_k \sim 1.7$ nm. OAPS experiences strong hydrogen-bonding attractions with *both* itself and P2VP, with the latter allowing good dispersion. Details concerning sample preparation, characterization, and experimental protocol are presented in the Methods Section and Supplementary Information (SI).

Small angle X-ray Scattering (SAXS) has been used to analyze the OAPS dispersion in the nanocomposites. Detailed scattering data of all P2VP/OAPS are presented in the Figure S1 in SI. Fig. 1a shows representative scattering intensity data I(q) of OAPS in P2VP/OAPS (at $\varphi_{OAPS} = 18$ vol% and 37 vol%) obtained after subtracting the volume fraction weighted scattering of pure P2VP melt. These results reveal excellent NP dispersion up to ~27 vol%, that can be fit by fuzzy sphere model (details of the fit procedure are presented in SI). A representative static structure factor S(q) of OAPS in P2VP ($\varphi_{OAPS} = 18$ vol%), converted from the scattering intensity I(q) following the procedure proposed by Jouault *et al.*²⁵⁻²⁶ (for details see SI), shows a low q plateau value of ~1 (inset Fig.1a) which further supports dispersion at the single NP level. An increase of scattering intensity at low q (q<0.02 Å⁻¹) for $\varphi_{OAPS}=37$ vol% (Fig.1a) and higher is observed, indicating some spatial heterogeneity due to

aggregation and/or kinetic gelation,²⁷ although the samples remain optically transparent up to $\varphi_{OAPS} \sim 54 \text{ vol}\%$.



Figure 1 Reduced small angle X-ray scattering for P2VP/OAPS with $\varphi_{OAPS} = 18$ vol% and $\varphi_{OAPS} = 37$ vol%. The black lines show a fit to a fuzzy sphere model for $\varphi_{OAPS} = 18$ vol%, and a combination of a power law and the fuzzy sphere model for $\varphi_{OAPS} = 37$ vol% (for details see SI). The inset shows the corresponding static structure factor S(q) ($\varphi_{OAPS} = 18$ vol%). (b) The chemical structure of OAPS, where the amine group can form H-bonding with both P2VP segments and OAPS particles themselves.

Broadband dielectric spectroscopy (BDS) was employed to probe segmental dynamics in these PNCs. The BDS data reveal large changes in the α -process peak with NP loading (Fig.2a): (i) a shift to lower frequency, (ii) broadening, (iii) decreased amplitude. The segmental relaxation time is estimated from the peak frequency, $\tau_{\alpha}=1/(2\pi f_p)$, and exhibits an unusually strong slowing down relative to the neat polymer at low temperatures (up to 6 decades at T ~ 410 K), which decreases to less than 1 decade at high temperatures (Fig.2b). The data also reveal a dramatic increase in T_g (defined by τ_{α} = 100 s) of up to ~35 K.



Figure 2 (a) Representative dielectric spectra of P2VP/OAPS with different loadings (in vol%) at 453 K where the structural relaxation α -peak is well-defined. (b) Temperature dependence of τ_{α} for neat P2VP and P2VP/OAPS PNCs with different loadings.

Temperature differential scanning calorimetry modulated (TMDSC) measurements provide thermodynamic estimates of Tg. It is worth noting that there are no transition steps in DSC data of neat OAPS for T=313K-453K (Fig.S2 in SI), signifying its high melting temperature or Tg. The PNC Tg, defined as the mid-point of the transition step, shifts from 372 K to 407 K (Fig.3), consistent with the BDS measurements. This is an extraordinarily large increase compared to conventional PNCs with similar loading, e.g., P2VP/SiO₂ (D = 25 nm) exhibits T_g shifts of only ~2-5 K (Figs.3 and 5a).^{8, 10} The step amplitude, ΔC_p , of the P2VP/OAPS PNCs reveals another anomaly (Fig.5b): it remains almost constant ~ 0.27 J/(gK) despite a strong decrease in polymer weight fraction, which is again in qualitative contrast to conventional PNCs where ΔC_p scales well with polymer fraction (inset Fig.5b).^{8, 10}



Figure 3 Temperature modulated differential scanning calorimetry measurements data of P2VP/OAPS nanocomposites with different loadings. Inset shows results for P2VP/SiO₂ with nanoparticle D ~ 25 nm (φ_{SiO2} =0 vol%, 16 vol%, and 35 vol%).

Rheology was employed to measure linear viscoelastic responses of both P2VP/OAPS and P2VP/SiO₂ PNCs. We used small amplitude oscillatory shear measurements, and the master curves of G'(ω) and G" (ω) spectra have been constructed using time-temperature superposition principles (Fig.S3). Fig.4a presents the G'(ω) and G"(ω) spectra of neat P2VP melt, P2VP/OAPS with $\varphi_{OAPS} = 27$ vol%, and the conventional P2VP/SiO₂ with $\phi_{SiO_2} = 27$ vol%, at T_{ref} = 453 K. The conventional P2VP/SiO₂ PNC shows the common gelation behavior, as indicated by a low frequency power law G'~G"~ $\omega^{0.25}$, strong enhancement of the modulus, and absence of terminal flow³ (Fig. 4a). The rheological behavior of P2VP/OAPS at a similar loading is remarkably different and unexpected (Fig. 4a): (i) the entanglement plateau modulus is almost identical to that of neat P2VP; (ii) intermediate frequency (Rouse) dynamics are significantly slower, with an entanglement onset time, τ_e , ~11 times longer than in neat P2VP despite τ_α increasing only by a factor of ~1.9; (iii) the terminal flow time τ_d increases only by a factor of ~1.2. Consequently, the

entanglement plateau breadth, quantified by τ_d/τ_e , shrinks from ~700 (neat P2VP), to ~70 at $\phi_{OAPS}=27$ vol%, and to only ~5 at $\phi_{OAPS}=37$ vol% (Fig. 4a and Fig.S3 in SI) indicating an apparent "disentanglement" in P2VP/OAPS. (iv) The complex viscosity, $|\eta^*|$, (inset Fig. 4a) shows a zero-shear-rate plateau comparable to neat P2VP, in a sharp contrast to the ~1000 times increase for the conventional P2VP/SiO₂ PNC. Interestingly, the P2VP/OAPS nanocomposites do show gel-like behavior at loadings exceeding 43 vol% (Figs. 4b and S3). Kinetic gelation in nanocomposites requiring such a high loading (especially for small NPs) is unexpected in the context of traditional PNCs.²⁸ However, a detailed discussion of the gelation behavior is beyond the scope of the current paper and will be considered in a future publication.



Figure 4 (a) Master curves constructed by time-temperature superposition of G' and G" of P2VP/SiO₂ ($\phi_{SiO2} = 27 \text{ vol}\%$, pink and purple symbols), P2VP/OAPS ($\phi_{OAPS} = 27 \text{ vol}\%$, olive, black symbols) and neat P2VP (red, blue lines) at $T_{ref} = 453$ K. Inset shows the complex viscosity, $|\eta^*|$, of neat P2VP (red), P2VP/OAPS (blue), and P2VP/SiO₂ (olive). (b) Master curves at $T_{ref} = 453$ K constructed using time-temperature superposition of G' and G" for neat P2VP (red and blue lines), P2VP/OAPS ($\phi_{OAPS} = 37 \text{ vol}\%$) (diamonds and upper triangles), and P2VP/OAPS ($\phi_{OAPS} = 54 \text{ vol}\%$) (down triangles and hexagons).



Figure 5 (a) Shift in T_g, Δ T_g, (b) specific heat capacity jump at T_g, and (c) fragility index as a function of loading for P2VP/OAPS (red circles) and P2VP/SiO₂ (D_{SiO2} = 25 nm) (blue squares). (d) entanglement plateau length τ_d/τ_e , (e) entanglement to alpha time ratio, τ_e/τ_α , and (f) τ_d/τ_α ratio of P2VP/OAPS PNCs at different loadings. Inset in (b) shows Δ C_p of the matrix, $C_p^{mat} = \frac{C_p^{PNC} - C_p^{NP} m_{NP}}{1 - m_{NP}}$, appears to be independent of loading in the conventional

PNCs, where C_p^{NP} and m_{NP} are the specific heat capacity and weight fraction of the NPs, respectively. The blue line in (d) is the dilution prediction of reptation-tube theory.²⁹

DISCUSSION

The presented experimental results reveal unexpectedly large and unusual effects of small sticky nanoparticles on segmental dynamics, T_g, thermodynamic properties, and viscoelastic response of PNCs. There are 7 key points.

(i) There is a dramatic increase in T_g , of up to ~35 K, which is seen in *both* BDS and thermodynamic measurements (Fig.5a). This is in sharp contrast to a ~ 2-5 K increase in conventional P2VP/SiO₂ (D = 25 nm) PNCs¹⁰

ACS Nano

(Fig.5a), as well as another polymer/POSS nanocomposites that showed a reduction in T_g due to plasticizer effect of small nanoparticles.³⁰

(ii) The temperature dependence of τ_{α} is usually quantified by the fragility

index,
$$m = \frac{d \left[\log_{10} \tau(T) \right]}{d(T_g / T)} \Big|_{T = T_g}$$
. Remarkably, it grows enormously from m

= 100 for neat P2VP to m = 270 for $\varphi_{OAPS} = 54$ vol% (Fig.5c), compared to a tiny ~ 10% change observed in conventional P2VP/SiO₂ PNCs (Fig.5c). Moreover, m = 270 is much higher than any value ever reported for polymer melts,³¹ implying a sharp slowing down of dynamics with cooling and unusual glass-formation behavior of PNCs with small attractive NPs.

- (iii) The specific heat capacity jump of the PNCs, ΔC_p^{PNC} , is almost independent of loading in P2VP/OAPS (Fig. 3), while in P2VP/SiO₂ (D = 25 nm) PNCs it monotonically decreases with loading. This strongly suggests that small nanoparticle mobility contributes in an essential manner to the kinetic vitrification and thermodynamics of OAPS-based PNCs.
- (iv) The kinetic gelation that occurs in the conventional $P2VP/SiO_2$ (D = 25 nm) PNC, is absent in P2VP/OAPS even at very high loading.
- (v) Intriguingly, the breadth of the entanglement rubbery plateau, quantified by the time ratio τ_d/τ_e , decreases almost exponentially with loading (Fig. 5d), $\tau_d/\tau_e \propto \exp(-13\varphi_{NP})$. This is much stronger than a power law dilution effect typically seen with addition of solvent or tiny nanoparticles (blue line in Fig. 5d).²⁹

ACS Paragon Plus Environment

- (vi) The ratio of the entanglement onset time to the structural relaxation (alpha) time, τ_e/τ_{α} , also increases exponentially with loading (Fig. 5e), $\tau_e/\tau_{\alpha} \propto \exp(13\varphi_{NP})$. This violates the traditional idea that changes of segmental and chain modes with nanoparticle addition are fully coupled.
- (vii) In contrast to points (v) and (vi), the ratio τ_d/τ_{α} is almost loading independent (Fig. 5f), implying the dependence of the flow time and viscosity enhancements on loading are controlled entirely by the alpha relaxation.

All these experimental results clearly demonstrate that P2VP/OAPS PNCs are in many respects qualitatively different from conventional PNCs^{3, 10-13, 32} (Fig.5). Defining physical features of the latter such as effectively immobile nanoparticles, the formation of nanoscopic "bound adsorbed layers" on the surface of large NPs, and decoupling of dynamic and psuedo-thermodynamic measures of vitrification, are not applicable.¹⁸

To gain deeper insight, we performed coarse-grained molecular dynamics simulations (see Methods and SI for details) where the NP and polymer segment have identical size and attract with an energy of 2-4 k_BT. The NP-NP and polymer-polymer interactions are repulsive, ensuring miscibility. The key findings are (Fig.6): (i) Nanoparticles and segments have comparable structural relaxation times, $\tau_{NP}=1\sim 2 \tau_{\alpha}$, suggesting a very strong coupling of segment and NP motions, in qualitative contrast to conventional PNCs where nanoparticles are essentially immobile on the segmental time scale. (ii) The time scale for relative NP-segment motion ("dissociation time"),

 τ_{dis} , estimated from the dynamic cross correlation function (see SI), is slower than the alpha process, increasing to $\tau_{dis} \sim 10^2 \cdot 10^3 \tau_{\alpha}$ for the strongest attraction. This suggests complete PNC structural relaxation involves two processes: cage relaxation and breaking of NP-polymer bonds, with the latter being slower.

Detailed comparisons of simulation with experiment is inappropriate because the simulations are not in the deeply supercooled regime and NP-NP attraction is not included. To understand the deeply supercooled regime, we apply the recently developed "Elastically Collective Nonlinear Langevin Equation" (ECNLE) approach, a quantitative theory of one-component molecular and polymer liquids.³³ Here it is extended to treat a binary mixture of equal-sized NP and segment spheres to study their cooperative activated hopping building on ideas successfully developed for colloidal mixtures³⁴ (see Methods and SI). For physical context, the inset of Fig.7a sketches the P2VP/OAPS PNC of interest and shows that at the relatively high loadings of primary interest essentially every polymer segment is in contact with one or more NPs. Two attraction energy parameters (defined relative to the segmentsegment attraction as a reference), between a segment and NP and between two NPs, ε_{pn} and ε_{nn} , respectively, are introduced. Their values are chosen based on chemical knowledge ($\epsilon_{pn} < \epsilon_{nn}$) and to ensure miscibility. Details of the model, mapping and theory are presented in the Methods and the SI.



Figure 6 Simulation results for (a) normalized alpha relaxation time of polymer segments $(\tau_{polymer}/\tau_{\alpha}(\phi_{NP}=0), \text{ symbols})$ and nanoparticles $(\tau_{NP}/\tau_{\alpha}(\phi_{NP}=0), \text{ lines})$; and (b) normalized nanoparticle – segment dissociation time $(\tau_{dis}/\tau_{\alpha}(\phi_{NP}))$ as a function of loading at different polymer-nanoparticle interaction strength. At $\varepsilon=1$ k_BT the interactions are purely repulsive while the other ε 's have attractions. See SI for details.



Figure 7 (a) Mean collective alpha time as a function of inverse temperature for mixtures ($\varepsilon_{pn} = 0.25$, $\varepsilon_{nn} = 0.75$ in thermal energy units with T = 571 K) with various NP loading φ_n . Inset: Realistic sketch of the PNC with equal sized NP and Kuhn segment at $\varphi_n=33$ vol%. (b) Glass transition temperature shift and fragility index (inset) predictions for various attraction strength parameters (lines), compared to experiment (symbols).

Figure 7a shows theoretical calculations of the PNC mean alpha relaxation time for a specific choice of attraction energies at different loadings over a wide temperature range. By accounting for coupled activated motion of segments and nanoparticles (which is predicted to occur on essentially the same mean time scale, see SI), the theory qualitatively captures the basic experimental features (Fig. 2b).

Predictions for how the alpha time increases with NP loading at fixed temperature are given in the SI. Fig. 7b shows the T_g shift and fragility index results corresponding to Fig.7a for several different choices of attraction energies. They agree well with the large increases observed experimentally, including the distinctive nearly linear growth of T_g with loading. More broadly, the theoretical results illustrate how dynamic properties can be widely tuned by manipulating chemically-specific attractions.

The physical picture that emerges from a detailed theoretical analysis (see SI) is that modestly sticky NPs form a limited number of physical bonds between themselves and with the polymer, resulting in extra dynamical constraints beyond steric caging, which increases the activation barrier, $\alpha\text{-relaxation}$ time and T_g . The T_g shifts grow as either ε_{pn} or ε_{nn} increase. However, the correctly predicted roughly linear growth of T_g with loading does *not* occur if one unrealistically sets $\varepsilon_{nn}=0$, and thus NP-NP transient physical bond formation appears to be critical for the observed effects. The enhanced fragility has a structural and thermodynamic origin: as loading increases, more temperature sensitive physical bonds form and the growth of the PNC total packing fraction with cooling is enhanced. Importantly, a key idea suggested by theory and simulation that the alpha process involves cooperative motion of segments and nanoparticles immediately provides a basis to understand the negligible change in the PNC heat capacity jump, ΔC_p , with loading (Figs. 3 and 5b). The contribution of small NP motion to the specific heat compensates the lost of polymer weight fraction. We emphasize that the near equality of segment and NP relaxation time scales is a consequence of both the relatively weak nature of the attractive interactions (and

corresponding modest cohesive energy, see SI) and the highly limited number of bonds a NP can form with the polymer given its small size. Either one or both of these features are absent in traditional PNC's which have well-defined, generally strongly bound layers of a \sim 1-5 nm thick,⁹⁻¹¹ typically resulting in a large time scale separation between NP motion and segmental relaxation.

Given NP and segmental motions are strongly coupled, it seems unlikely (all) physical bonds are broken by the alpha process, suggesting a longer time scale for complete structural re-arrangement and initiation of chain-scale motion (e.g., Rouse, reptation). Such a bond dissociation process can lead to a two step structural relaxation (cage escape and bond breaking) in dense attractive colloid suspensions³⁵ and associating polymer liquids.³⁶⁻³⁷ We expect the dissociation time $\tau_{dis}(\phi_{NP}) >$ $\tau_{\alpha}(\phi_{\rm NP})$ and its ratio grows with loading, as suggested by simulation (Fig.6). Although the precise mechanism is unclear, we explore a simple physical idea, generically motivated by "sticky Rouse" models.³⁶⁻³⁷ We postulate $\tau_{dis} \sim \tau_{\alpha} \exp(U_{NP}/k_BT)$, where the structural theory predicts the cohesive energy per particle $U_{NP} \propto \phi_{NP}$ and $\tau_{e}(\phi_{NP}) \propto \tau_{dis} \sim \tau_{\alpha}(\phi_{NP}) \exp(b\varphi_{NP})$ with b~7-13 (see SI). The exponential enhancement of the entanglement onset time relative to the alpha time, and the magnitude of b, are consistent with experiment (Fig.5e). However, naively, this idea would seem to predict a stronger dependence of the flow time on loading than the alpha time, which is not observed (Fig.5f). One possiblity is the slowing down of Rouse modes due to *small* sticky particles is a frictional effect which does not modify entanglement elastic properties. This speculation is consistent with our $\tau_e(\phi_{NP})$ data (Fig.5e), and the

ACS Nano

loading independence of both $\tau_d(\varphi_{NP})/\tau_\alpha(\varphi_{NP})$ (Fig.5f) and the plateau modulus. More study is needed to draw definitive conclusions. But, the rheological behavior clearly does not follow standard "sticky Rouse"³⁶⁻³⁷ or "sticky reptation"³⁸ models, where the terminal time grows due to a long "sticker lifetime". It also differs drastically from conventional PNCs (Fig.4) where nonequilibrium effects are caused by the exceptionally long chain-nanoparticle desorption times (~10⁶-10¹² τ_α).³⁹

CONCLUSIONS

Our studies reveal qualitatively different behaviors of PNC dynamics when nanoparticles are sticky and comparable in size to a polymer segment. The tunable range of T_g and fragility far exceeds that previously found for conventional PNCs, while thermodynamic and viscoelastic properties show qualitatively unexpectedly small changes. We suggest all these results reflect the relatively fast mobility of small and moderately attractive NPs on the time scale of segmental dynamics which arises from the facile dissociation of the relatively weak and highly limited number of physical bonds between nanoparticles and segments. The absence of significant viscosity change at high temperatures renders these PNCs very attractive in applications and processing. Our results suggest exciting opportunities for tuning macroscopic properties of PNCs over a range inaccessible with conventional PNCs by (i) controlling nanoparticle mobility *via* their size (in contrast to relatively immobile larger NPs), and (ii) by tuning the strength and lifetime of physical bonds *via* the rational chemical manipulation of attractive forces.

METHODS

Materials and sample preparations. Tetrahydrofuran (THF) was purchased from Sigma-Aldrich and used as received. Octaaminophenyl polyhedral oligomeric silsesquioxane (OAPS) was purchased from SES materials and used as received. Poly(2-vinylpyridine) (P2VP) with molecular weight (M_W) of 101 kg/mol and polydispersity of 1.07 was purchased from Scientific Polymer Source Inc. The OAPS powder was first dissolved in THF to prepare a stock solution of 0.15 g/ml. For polymer nanocomposites of each type, 0.3 g of polymers were first dissolved in 10 ml of THF to form polymer/THF solutions. Then, different amounts of OAPS/THF solution were added and mixed for 1 hour. After that, the polymer/OAPS naocomposite solutions were poured into a teflon dish to first dry under a hood for 24 hours before transferred to a vacuum oven (10⁻⁶ bar) under 160 °C for one more week. All the samples were characterized by thermogravimetric analysis (TGA) (TA instrument Discover Q 50) under air with 20 °C/min heating up to 800 °C, and temperature modulated differential scanning calorimetry (TMDSC) (TA instrument, Q2000) with heating/cooling rate of 2 °C/min and modulation speed of ± 0.5 °C/min. Mass densities of OAPS, SiO₂ nanoparticles, and neat P2VP were 1.4028 \pm 0.0019 g/cm^3 , 2.4057 \pm 0.0019 g/cm^3 , and 1.2249 \pm 0.0024 g/cm^3 , respectively, and were measured by gas pycnometry (Micromeretics Accupyc II 1340).

Broadband Dielectric Spectroscopy (BDS) Measurements in the frequency range

ACS Paragon Plus Environment

 $10^{-2} - 10^{7}$ Hz were carried out using a Novocontrol Concept-80 system with an Alpha-A impedance analyzer, a Quatro Cryosystem temperature controller and a ZGS sample holder. PNC films of 0.08-0.15 mm were hot-pressed at 160 °C for P2VP/OAPS nanocomposites in a teflon ring with inner diameter of 14 mm and outer diameter of 24 mm. These samples were then sandwiched by two gold-coated electrodes with diameter of 20 mm before being transferred to the ZGS sample holder. All the measurements were conducted in the temperature range 473 K – 273 K with a step of 5 K between 473K and 363 K and 10 K between 363 K and 273 K. A thermal equilibration of 20 minutes was performed at each temperature before measurements.

Shear Rheology: Small amplitude oscillatory shear (SAOS) measurements were conducted on an AR2000ex rheometer (TA Instrument). For segmental relaxation and the glassy modulus, a parallel plate of 4 mm in diameter and a strain amplitude of 0.05 % were used. For rubbery plateau and terminal relaxation measurements, a parallel plate of 8 mm in diameter and a strain amplitude of 1.0 % was used. The temperature was controlled by an environmental test chamber under nitrogen atmosphere. The accuracy of the temperature was ± 0.1 °C.

Small angle X-ray Scattering (SAXS) measurements were performed at the Duke Shared Materials Instrumentation Facility using a high flux small angle X-ray scattering instrument (SAXSLab Ganesha), a point collimated pinhole system with a 2D configurable detector and a Cu 50kV Xenocs Genix ULD SL X-ray Source. All

the measurements were performed at room temperature in transmission geometry on a series of thin nanocomposite films for a range of OAPS loadings. Scattering intensities measured as a function of half the scattering angle, θ , were first corrected for the absorption of the X-rays by the sample followed by further correction for the scattering of the empty cell and transformed to a plot of absolute scattering intensity vs. momentum transfer vector, q ($q = 4\pi \sin \theta / \lambda$). The corrected data were normalized to absolute units with respect to the scattering of a water sample that is measured at exactly the same conditions as the P2VP/OAPS nanocomposite samples.

Molecular Dynamics Simulations: Coarse-grained (CG) molecular dynamics (MD) simulations based on the polymer melt model by Kremer and Grest⁴⁰ but modified to include sticky nanoparticles, were performed at the Oak Ridge Leadership Computing Facility (OLCF) using the LAMMPS⁴¹⁻⁴² software package. The simulations contain 500 polymer chains with degree-of-polymerization of N=400 which are mixed with varying amounts of sticky nanoparticles of up to 25% by volume. Initially, the neat polymer melt was equilibrated using a combination of molecular dynamics simulations and Monte Carlo bond swaps.⁴³ Thereafter, several copies of the equilibrated polymer melt were inserted with small nanoparticles at random locations resulting to several systems with different nanoparticle loading. These were then equilibrated by slowly pushing off nanoparticles that overlap with polymer segments in an equilibration MD run and followed by an equilibration MD run of $10^5 \tau$ and a production MD run of $4 \times 10^5 \tau$. The resulting particle trajectories were used to

ACS Nano

calculate the self-intermediate dynamic structure factor $F_s(t)$ and the cross-correlation function between polymer segments and nanoparticles $F_{12}(q,t)$. More details on the simulations and analysis of the simulation results are presented in the SI.

Theory: We considered two structural models of a P2VP/OAPS nanocomposite as a mixture of spherical hard nanoparticles with polymers represented as either Kuhn length sized hard spheres or freely jointed chains (FJC) composed of *N* segments. Kuhn spheres or segments are equal in diameter to nanoparticles to mimic the P2VP/OAPS system. When polymers are mapped to a liquid of either disconnected Kuhn-sized hard spheres or connected FJCs, their temperature-dependent (at 1 atm) dimensionless compressibilities are required to be identical to the experimentally known value.³³ As nanoparticles are added, because the equation-of-state (EOS) of the P2VP/OAPS mixture is not experimentally available, we adopt two "calibration" strategies without introducing any adjustable parameters: keep the mixture bulk modulus *K_B* or the pressure *p* constant. Details are in the SI.

Nanoparticles attract each other and the polymer segments *via* the pair potential:

$$U_{nj}\left(r\right) = -\varepsilon_{nj}e^{-(r-D)\alpha D}, r \ge \sigma_{nj}, j = n, p \qquad (M.1)$$

where α is a dimensionless spatial range parameter (set to 0.1 to mimic short range hydrogen bonding attractions). The choice of ε_{np} and ε_{nn} is described in the SI. The interaction between polymer segments is pure hard core $\varepsilon_{pp} = 0$. The structural pair correlation functions and static structure factors required to implement the

dynamical theory are computed using standard Ornstein-Zernike integral equation theory⁴⁴ for the sphere mixture model and PRISM integral equation theory⁴⁵ when polymers are mapped to FJCs. The site-site Percus-Yevick closure approximation is adopted for all direct correlation functions.

The mixture nonlinear Langevin equation (NLE) theory³⁴ has been adopted to study the dynamics of P2VP/OAPS mixture. The key quantity is the so-called dynamic free energy surface as a function of displacement of the two species from their transiently localized positions ($\delta r_p = \delta r_n = 0$), $\delta r_n / \delta r_p$; it can be constructed from knowledge of the pair correlation structure of the mixture. The most important feature is the barrier height F_B along different path $\delta r_n / \delta r_p$. A representative calculation is shown in the SI. While it is now well established that NLE theory is a dynamic mean field approach that captures only the local caging aspect of the activated relaxation process and significantly under predicts barriers in deeply supercooled liquid,^{33, 46} the "Elastically Collective Nonlinear Langevin Equation" (ECNLE) theory for one component system has been developed^{33, 46} to include longer range collective effects based on the physical idea that elastic distortion of the surrounding liquid is required to allow relatively large amplitude particle hopping on the cage scale.^{33, 46} We straightforwardly extend this idea to mixtures to calculate the required collective elastic barrier $F_{elastic}$ (see SI). We find that, in accord with our physical intuition, the global minimum of the total barrier height $F_{total} (\equiv F_B +$ $F_{elastic}$) is very close to $\delta r_n / \delta r_p = 1.0$ when polymers are mapped to either an effective hard sphere fluid or FJCs. Thus, the "most collective" trajectory path

ACS Nano

 $\delta r_n / \delta r_p = 1.0$ is adopted to calculate the α relaxation time for all models under all conditions in this paper.

The mean barrier hopping time, which represents a collective hop of the two species following the maximally cooperative trajectory, follows as^{33, 46}

$$\tau_{\alpha} = \tau_{s} \left[1 + \frac{2\pi}{\sqrt{K_{0}K_{B}}} e^{\beta \left(F_{B} + F_{elastic}\right)} \right], \qquad (M.2)$$

where K_0 and K_B are the absolute magnitudes of well and barrier positive curvature constants of units of $k_B T/\sigma^2$, respectively. The mean barrier hopping time is closely correlated with the structural alpha relaxation time⁴⁷. For simplicity, τ_s is set to the realistic value of 10 ps, analogous to prior one-component liquid calculations.⁴⁶ We define T_g as when τ_{α} equals 100s. Dynamic fragility *m* is computed using the standard definition and our theoretically computed temperature-dependent alpha relaxation time.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Detailed analysis of the small angle X-ray scattering data; Temperature modulated differential scanning calorimetry measurement of neat OAPS; Master curves of loss and storage spectra from small amplitude oscillatory shear measurements; Details of computer simulations and additional results; Detailed descriptions of theory and additional results.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Science, Basic

Energy Sciences, Materials Science & Engineering Division.

AUTHOR CONTRIBUTIONS

S.C., B.C. and A.S. carried out and designed the experiments. H.M. and M.D

performed and analyzed the SAXS measurements. S-J.X. and K.S. carried out the

theoretical calculations. J-M.C. and B.S. performed the computer simulations. All

authors contributed to the writing of the manuscript.

REFERENCES:

- Bansal, A.; Yang, H. C.; Li, C. Z.; Cho, K. W.; Benicewicz, B. C.; Kumar, S. K.; Schadler, L. S., Quantitative Equivalence between Polymer Nanocomposites and Thin Polymer Films. *Nat. Mater.* 2005, *4*, 693-698.
- Rittigstein, P.; Priestley, R. D.; Broadbelt, L. J.; Torkelson, J. M., Model Polymer Nanocomposites Provide an Understanding of Confinement Effects in Real Nanocomposites. *Nat. Mater.* 2007, *6*, 278-282.
- Baeza, G. P.; Dessi, C.; Costanzo, S.; Zhao, D.; Gong, S.; Alegria, A.; Colby, R. H.; Rubinstein, M.; Vlassopoulos, D.; Kumar, S. K., Network Dynamics in Nanofilled Polymers. *Nat. Commun.* 2016, 7, 11368.
- 4. Balazs, A. C.; Emrick, T.; Russell, T. P., Nanoparticle Polymer Composites: Where Two Small Worlds Meet. *Science* **2006**, *314*, 1107-1110.
- Hussain, F.; Hojjati, M.; Okamoto, M.; Gorga, R. E., Review Article: Polymer-Matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview. J. Compos. Mater. 2006, 40, 1511-1575.
- Jancar, J.; Douglas, J. F.; Starr, F. W.; Kumar, S. K.; Cassagnau, P.; Lesser, A. J.; Sternstein, S. S.; Buehler, M. J., Current Issues in Research on Structure-Property Relationships in Polymer Nanocomposites. *Polymer* 2010, *51*, 3321-3343.
- Papon, A.; Montes, H.; Hanafi, M.; Lequeux, F.; Guy, L.; Saalwächter, K., Glass-Transition Temperature Gradient in Nanocomposites: Evidence from Nuclear Magnetic Resonance and Differential Scanning Calorimetry. *Phys. Rev. Lett.* 2012, 108, 065702.
- 8. Moll, J.; Kumar, S. K., Glass Transitions in Highly Attractive Highly Filled Polymer Nanocomposites. *Macromolecules* **2012**, *45*, 1131-1135.
- Jouault, N.; Moll, J. F.; Meng, D.; Windsor, K.; Ramcharan, S.; Kearney, C.; Kumar, S. K., Bound Polymer Layer in Nanocomposites. *ACS Macro Letters* 2013, 2, 371-374.

- Holt, A. P.; Griffin, P. J.; Bocharova, V.; Agapov, A. L.; Imel, A. E.; Dadmun, M. D.; Sangoro, J. R.; Sokolov, A. P., Dynamics at the Polymer/Nanoparticle Interface in Poly(2-Vinylpyridine)/Silica Nanocomposites. *Macromolecules* 2014, 47, 1837-1843.
- Gong, S.; Chen, Q.; Moll, J. F.; Kumar, S. K.; Colby, R. H., Segmental Dynamics of Polymer Melts with Spherical Nanoparticles. *ACS Macro Letters* 2014, *3*, 773-777.
- Cheng, S.; Holt, A. P.; Wang, H.; Fan, F.; Bocharova, V.; Martin, H.; Etampawala, T.; White, B. T.; Saito, T.; Kang, N.-G., *et al.*, Unexpected Molecular Weight Effect in Polymer Nanocomposites. *Phys. Rev. Lett.* **2016**, *116*, 038302.
- Holt, A. P.; Bocharova, V.; Cheng, S.; Kisliuk, A. M.; White, B. T.; Saito, T.; Uhrig, D.; Mahalik, J. P.; Kumar, R.; Imel, A. E., *et al.*, Controlling Interfacial Dynamics: Covalent Bonding Versus Physical Adsorption in Polymer Nanocomposites. *ACS Nano* 2016, *10*, 6843-6852.
- 14. Berriot, J.; Montes, H.; Lequeux, F.; Long, D.; Sotta, P., Evidence for the Shift of the Glass Transition near the Particles in Silica-Filled Elastomers. *Macromolecules* **2002**, *35*, 9756-9762.
- 15. Schadler, L. S.; Kumar, S. K.; Benicewicz, B. C.; Lewis, S. L.; Harton, S. E., Designed Interfaces in Polymer Nanocomposites: A Fundamental Viewpoint. *MRS Bull.* **2007**, *32*, 335-340.
- Papon, A.; Montes, H.; Lequeux, F.; Oberdisse, J.; Saalwachter, K.; Guy, L., Solid Particles in an Elastomer Matrix: Impact of Colloid Dispersion and Polymer Mobility Modification on the Mechanical Properties. *Soft Matter* 2012, *8*, 4090-4096.
- Cheng, S.; Bocharova, V.; Belianinov, A.; Xiong, S.; Kisliuk, A.; Somnath, S.; Holt, A. P.; Ovchinnikova, O. S.; Jesse, S.; Martin, H., *et al.*, Unraveling the Mechanism of Nanoscale Mechanical Reinforcement in Glassy Polymer Nanocomposites. *Nano Lett.* **2016**, *16*, 3630-3637.
- Starr, F. W.; Douglas, J. F.; Meng, D.; Kumar, S. K., Bound Layers "Cloak" Nanoparticles in Strongly Interacting Polymer Nanocomposites. *ACS Nano* 2016 DOI: 10.1021/acsnano.6b05683.
- Tuteja, A.; Mackay, M. E.; Narayanan, S.; Asokan, S.; Wong, M. S., Breakdown of the Continuum Stokes–Einstein Relation for Nanoparticle Diffusion. *Nano Lett.* 2007, 7, 1276-1281.
- Cai, L.-H.; Panyukov, S.; Rubinstein, M., Mobility of Nonsticky Nanoparticles in Polymer Liquids. *Macromolecules* 2011, 44, 7853-7863.
- Yamamoto, U.; Schweizer, K. S., Microscopic Theory of the Long-Time Diffusivity and Intermediate-Time Anomalous Transport of a Nanoparticle in Polymer Melts. *Macromolecules* 2015, 48, 152-163.
- 22. Nusser, K.; Schneider, G. J.; Pyckhout-Hintzen, W.; Richter, D., Viscosity Decrease and Reinforcement in Polymer–Silsesquioxane Composites. *Macromolecules* **2011**, *44*, 7820-7830.
- Kropka, J. M.; Sakai, V. G.; Green, P. F., Local Polymer Dynamics in Polymer-C-60 Mixtures. *Nano Lett.* 2008, *8*, 1061-1065.

24. Kuo, S.-W.; Chang, F.-C., Poss Related Polymer Nanocomposites. *Prog. Polym. Sci.* 2011, *36*, 1649-1696.

- Jouault, N.; Dalmas, F.; Said, S.; Di Cola, E.; Schweins, R.; Jestin, J.; Boué, F., Direct Small-Angle-Neutron-Scattering Observation of Stretched Chain Conformation in Nanocomposites: More Insight on Polymer Contributions in Mechanical Reinforcement. *Phys. Rev. E* 2010, *82*, 031801.
- Jouault, N.; Dalmas, F.; Said, S.; Di Cola, E.; Schweins, R.; Jestin, J.; Boué, F., Direct Measurement of Polymer Chain Conformation in Well-Controlled Model Nanocomposites by Combining Sans and Saxs. *Macromolecules* 2010, 43, 9881-9891.
- Akcora, P.; Liu, H.; Kumar, S. K.; Moll, J.; Li, Y.; Benicewicz, B. C.; Schadler, L. S.; Acehan, D.; Panagiotopoulos, A. Z.; Pryamitsyn, V., *et al.*, Anisotropic Self-Assembly of Spherical Polymer-Grafted Nanoparticles. *Nat. Mater.* 2009, *8*, 354-U121.
- Chen, Q.; Gong, S.; Moll, J.; Zhao, D.; Kumar, S. K.; Colby, R. H., Mechanical Reinforcement of Polymer Nanocomposites from Percolation of a Nanoparticle Network. ACS Macro Letters 2015, 4, 398-402.
- 29. Doi, M., and S.F. Edwards, *The Theory of Polymer Dynamics*. Oxford University Press, New York: 1986.
- Kopesky, E. T.; Haddad, T. S.; Cohen, R. E.; McKinley, G. H., Thermomechanical Properties of Poly(Methyl Methacrylate)S Containing Tethered and Untethered Polyhedral Oligomeric Silsesquioxanes. *Macromolecules* 2004, 37, 8992-9004.
- 31. Sokolov, A. P.; Novikov, V. N.; Ding, Y., Why Many Polymers Are So Fragile. J. *Phys. Condens. Matter* **2007**, *19*, 205116.
- Cheng, S.; Mirigian, S.; Carrillo, J.-M. Y.; Bocharova, V.; Sumpter, B. G.; Schweizer, K. S.; Sokolov, A. P., Revealing Spatially Heterogeneous Relaxation in a Model Nanocomposite. *J. Chem. Phys.* 2015, *143*, 194704.
- Mirigian, S.; Schweizer, K. S., Dynamical Theory of Segmental Relaxation and Emergent Elasticity in Supercooled Polymer Melts. *Macromolecules* 2015, 48, 1901-1913.
- Viehman, D. C.; Schweizer, K. S., Cooperative Activated Dynamics in Dense Mixtures of Hard and Sticky Spheres. *Phys. Rev. E* 2008, 78, 051404.
- Pham, K. N.; Puertas, A. M.; Bergenholtz, J.; Egelhaaf, S. U.; Moussaïd, A.; Pusey, P. N.; Schofield, A. B.; Cates, M. E.; Fuchs, M.; Poon, W. C. K., Multiple Glassy States in a Simple Model System. *Science* 2002, *296*, 104-106.
- Rubinstein, M.; Semenov, A. N., Dynamics of Entangled Solutions of Associating Polymers. *Macromolecules* 2001, 34, 1058-1068.
- Chen, Q.; Tudryn, G. J.; Colby, R. H., Ionomer Dynamics and the Sticky Rouse Model. J. Rheol. 2013, 57, 1441-1462.
- 38. Leibler, L.; Rubinstein, M.; Colby, R. H., Dynamics of Reversible Networks. *Macromolecules* **1991**, *24*, 4701-4707.
- 39. Napolitano, S.; Wubbenhorst, M., The Lifetime of the Deviations from Bulk Behaviour in Polymers Confined at the Nanoscale. *Nat. Commun.* **2011**, *2*, 260.

1
2
3
4
5
6
7
8
9
10
11
12
12
14
14
10
10
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
27
31
აი ეე
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
50
ວ/ E0
วช

59

- 40. Kremer, K.; Grest, G. S., Dynamics of Entangled Linear Polymer Melts: &Nbsp; a Molecular-Dynamics Simulation. J. Chem. Phys. **1990**, *92*, 5057-5086.
- 41. Plimpton, S., Fast Parallel Algorithms for Short-Range Molecular Dynamics. J. Comput. Phys. 1995, 117, 1-19.
- Brown, W. M.; Wang, P.; Plimpton, S. J.; Tharrington, A. N., Implementing Molecular Dynamics on Hybrid High Performance Computers–Short Range Forces. *Comput. Phys. Commun.* 2011, 182, 898-911.
- 43. Auhl, R.; Everaers, R.; Grest, G. S.; Kremer, K.; Plimpton, S. J., Equilibration of Long Chain Polymer Melts in Computer Simulations. *J. Chem. Phys.* **2003**, *119*, 12718-12728.
- 44. Hansen, J. P.; McDonald, I. R., *Theory of Simple Liquids*. Academic, London: 1986.
- 45. Hall, L. M.; Schweizer, K. S., Many Body Effects on the Phase Separation and Structure of Dense Polymer-Particle Melts. J. Chem. Phys. 2008, 128, 234901.
- Mirigian, S.; Schweizer, K. S., Elastically Cooperative Activated Barrier Hopping Theory of Relaxation in Viscous Fluids. Ii. Thermal Liquids. J. Chem. Phys. 2014, 140, 194507.
- 47. Schweizer, K. S.; Saltzman, E. J., Entropic Barriers, Activated Hopping, and the Glass Transition in Colloidal Suspensions. J. Chem. Phys. 2003, 119, 1181-1196.





