



HAL
open science

Enhancing the Mechanical Properties of Glassy Nanocomposites by Tuning Polymer Molecular Weight

Anne-Caroline Genix, Vera Bocharova, Alexander Kisliuk, Bobby Carroll,
Sheng Zhao, Julian Oberdisse, Alexei P. Sokolov

► **To cite this version:**

Anne-Caroline Genix, Vera Bocharova, Alexander Kisliuk, Bobby Carroll, Sheng Zhao, et al.. Enhancing the Mechanical Properties of Glassy Nanocomposites by Tuning Polymer Molecular Weight. ACS Applied Materials & Interfaces, 2018, 10 (39), pp.33601-33610. 10.1021/acsami.8b13109 . hal-01925066

HAL Id: hal-01925066

<https://hal.science/hal-01925066>

Submitted on 11 Jan 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Enhancing Mechanical Properties of Glassy Nanocomposites by Tuning Polymer Molecular Weight

Anne-Caroline Genix,^{1*} Vera Bocharova,^{2*} Alexander Kisliuk,² Bobby Carroll,² Sheng Zhao,³

Julian Oberdisse¹ and Alexei P. Sokolov^{2,3}

¹ *Laboratoire Charles Coulomb (L2C), Université de Montpellier, CNRS, F-34095 Montpellier, France*

² *Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

³ *Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA*

Corresponding Authors

*E-mail: anne-caroline.genix@umontpellier.fr

*E-mail: bocharovav@ornl.gov

KEYWORDS: Polymer nanocomposites, mechanical reinforcement, glass transition, segmental dynamics, interfacial layer

ABSTRACT

The addition of nanoparticles to a polymer matrix is a well-known process to improve mechanical properties of polymers. Many studies of the mechanical reinforcement in polymer nanocomposites (PNCs) focus on rubbery matrices; however, much less effort concentrates on factors controlling mechanical performance of the technologically important glassy PNCs. This paper presents a study of the effect of the polymer molecular weight (MW) on the overall mechanical properties of glassy PNCs with attractive interaction by using Brillouin light scattering. We found that the mechanical moduli (bulk and shear) have a non-monotonic dependence on MW that cannot be predicted by simple rule of mixtures. The moduli increase with increasing MW up to 100 kg/mol followed by a drop at higher MW. We demonstrate that the change in the mechanical properties of PNCs can be associated with the properties of the interfacial polymer layer. The latter depend on the interfacial chain packing and stretching, as well as polymer bridging that vary differently with MW of the polymer. These competing contributions lead to the observed non-monotonic variations of glassy PNC moduli with MW. Our work provides a simple, cost-effective, and efficient way to control the mechanical properties of glassy PNCs by tuning the polymer chain length. Our finding can be beneficial for rational design of PNCs with desired mechanical performance.

1
2
3
4
5
6 Polymer nanocomposites (PNCs) have become a prominent area of current research and
7
8 development. Addition of hard nanoparticles to a polymer matrix leads to a significant
9
10 improvement of several macroscopic properties, such as electrical ¹ or mechanical properties, ²⁻³
11
12 as well as reduction in membrane aging. ⁴ This makes PNCs attractive for various applications,
13
14 including surface coating, electronics, and gas separation membranes. In industry, combinatorial
15
16 methods are often used to design PNCs. These methods do not always lead to the desired
17
18 properties, highlighting the importance of a fundamental understanding of the factors affecting
19
20 macroscopic properties in PNCs. Our fundamental knowledge is rather limited with many open
21
22 questions, and especially those related to the microscopic origin of the mechanical reinforcement
23
24 found for PNCs in rubbery and in glassy states.⁵⁻¹⁰ Several mechanisms, such as particle jamming
25
26 ¹¹ and the formation of bridges between NPs,⁸⁻⁹ have been proposed to explain the increase in the
27
28 mechanical moduli in rubbery nanocomposites. However, much less is known about mechanical
29
30 enhancement in glassy PNCs due to the range of non-equilibrium states available for polymers,
31
32 and the limited number of experimental techniques to study viscoelastic, dynamic, and mechanical
33
34 properties of glassy polymers. Although the mechanical enhancement in a glassy PNC is large in
35
36 absolute values (a few GPa increase in modulus), the changes relative to the neat glassy polymer
37
38 are usually small (a few times),^{10, 12-14} and difficult to measure. Originally, the mechanical
39
40 enhancement in the glassy PNCs is interpreted by the hydrodynamic effect of the hard
41
42 nanoparticles. ¹⁵ This effect is due to the deformation of the flow field around the particle. It has
43
44 been shown by Smallwood ¹⁶ and Guth ¹⁷ that the force field on the polymer surrounding the
45
46 particle can be mapped on the flow field, leading to the same relative increase in modulus as given
47
48 by Einstein ¹⁸ for viscosity, i.e., $1 + 2.5 \Phi$ at low volume fractions Φ . However, recent mechanical
49
50 tests on glassy PNCs have clearly shown that mechanical reinforcement is stronger than predicted
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6 by the hydrodynamic approach.¹⁰ Besides, the dispersion state, i.e., the spatial arrangements of
7
8 the nanoparticles (NPs) within the matrix, has a strong impact on the mechanical performances.
9
10 Whereas the formation of a volume-spanning network of NPs, or NP aggregates might have
11
12 advantages in the melt state,¹⁹⁻²³ well-dispersed NPs are required to obtain optimal mechanical
13
14 properties below the glass-transition temperature, T_g .^{12, 24-25} This indicates that different
15
16 mechanisms contribute to the reinforcement in glassy and rubbery PNCs.
17
18
19
20

21
22 Recently, the concept of an interfacial polymer layer with a thickness of $\sim 2 - 6$ nm around the
23
24 nanoparticles and enhanced moduli has been employed to explain the mechanical properties of
25
26 PNCs in both the rubbery and glassy states.^{9-10, 26} For rubbery PNCs, a spatial dependence of the
27
28 viscoelastic modulus of the polymer chains has been proposed in relationship with the concept of
29
30 T_g -gradient.^{7, 27} In this approach, it is expected that the interfacial layer modulus will be about 10^2
31
32 $- 10^3$ times higher than that of the bulk rubbery polymer. This increase occurs because the adsorbed
33
34 polymer layer surrounding the nanoparticles displays an increased T_g in the case of attractive
35
36 polymer-filler interaction, and it might be in a glassy state even when the polymer matrix is still
37
38 in a rubbery state (above T_g). This leads to a higher mechanical moduli (glassy) with respect to the
39
40 neat polymer (rubbery moduli). Enhancement of the interfacial layer modulus has later been
41
42 confirmed via a direct nanoscale probing of the mechanical properties of the layer with atomic
43
44 force microscopy (AFM), where an increase of approximately one order of magnitude was found
45
46 with respect to the neat rubbery polymer.²⁸ In glassy PNCs, AFM measurements have also
47
48 indicated the presence of an interfacial layer with higher modulus than the neat polymer,^{10, 29} in
49
50 agreement with recent nanoindentation simulations³⁰. However, the data on the magnitude of the
51
52 elastic response as well as the extent of the interphase are usually very scattered,³⁰⁻³¹ which make
53
54
55
56
57
58
59
60

1
2
3
4
5
6 quantitative determinations of the local interfacial layer properties a challenging task when using
7
8 AFM. Therefore, other methods capable of investigating the mechanical properties at the interface
9
10 are required in glassy PNCs.
11
12
13

14
15 Brillouin light scattering (BLS) is a non-destructive optical technique based on the inelastic
16
17 scattering of visible light by thermal acoustic phonons, which can be used in both glassy and
18
19 rubbery PNCs.³² It allows accessing the velocity of sound in the system and therefore the elastic
20
21 properties (longitudinal and shear moduli) in the Gigahertz frequency range related to microscopic
22
23 length scales. Note that dynamic mechanical analysis or tensile tests provide macroscopic
24
25 properties, and are more sensitive to secondary relaxations, sample quality, and defects. Several
26
27 BLS studies have provided evidence of mechanical reinforcement in glassy PNCs.^{10, 32-34} It was
28
29 found that both the shear and bulk moduli increase with particle loading, and that this increase
30
31 cannot be explained by a two-phase model³⁵ assuming NPs dispersed in a homogeneous matrix.
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
10.²⁶ This discrepancy is a clear indication of an additional mechanism for reinforcement other than
the hydrodynamic effect, and it has been associated with the presence of an interphase with higher
modulus in the vicinity of the nanoparticles. The interfacial layer moduli were found to be about
2 times higher than that of the matrix using the interfacial layer model (ILM)³⁶ approach developed
for multi-component systems. On the other hand, other BLS studies have reported opposite
evolutions of the PNC elastic properties depending on the process conditions (solvent choice and
annealing),³³ or on the NP-polymer interaction using different types of surface modification, like
silanization³⁷ and chain grafting³⁸⁻³⁹. In particular, recently it has been found that a PNC with
grafted polymer chains displays lower moduli in the interfacial layer than in the case of PNC filled
with bare NPs, while still having a higher T_g and stronger suppression of the segmental dynamics.

1
2
3
4
5
6 ³⁹ Such a counter-intuitive behavior suggests a competition between different effects, namely
7
8 frustration in chain packing (density) and chain conformation (stretching) in the interfacial layer.
9
10 These effects can be varied by the polymer grafting density, and a low grafting density resulted in
11
12 a reduction of density and of the mechanical properties of the grafted PNCs. All these observations
13
14 highlight the prevalent role played by both the structural organization and dynamics of the
15
16 interfacial layer. In this context, the chain length or polymer molecular weight (MW) is an
17
18 important parameter. In PNCs with attractive interactions, both theoretical ⁴⁰ and experimental ⁴¹
19
20 studies have suggested that the chains form a physically adsorbed layer at the NP interface with
21
22 an average thickness proportional to the polymer radius of gyration. Such a bound layer gives rise
23
24 to a dynamic interfacial layer with different segmental dynamics ²⁶ and also different mechanical
25
26 properties than the bulk, as discussed above. Whereas one of our recent works report on the
27
28 unexpected MW-dependence of the interfacial layer thickness, which slightly decreases with
29
30 increasing chain length, ⁴² the evolution of elastic properties of the interfacial layer with MW has
31
32 never been studied to the best of our knowledge. Such studies of microscopic parameters
33
34 controlling macroscopic mechanical properties in glassy PNCs are highly desirable for both
35
36 fundamental research and practical applications.
37
38
39
40
41
42
43

44 This paper focuses on studies of the polymer molecular weight effect on the mechanical (bulk and
45
46 shear moduli) and dynamic properties of PNCs in the glassy state. We study a model
47
48 nanocomposite system based on poly(2-vinylpyridine) (P2VP) with a fixed loading of silica
49
50 nanoparticles (≈ 40 wt%), by combining Brillouin light scattering (BLS), small-angle X-ray
51
52 scattering (SAXS), broadband dielectric spectroscopy (BDS), and temperature-modulated
53
54 differential scanning calorimetry (TMDSC). We deliberately choose a high filler content to
55
56
57
58
59
60

1
2
3
4
5
6 achieve maximum enhancement of mechanical properties, while still maintaining reasonable
7
8 processability of the film, which is important for practical applications. Our analysis reveals that
9
10 the chain length has a strong influence on the resulting mechanical reinforcements in PNCs below
11
12 T_g . PNCs with low MW exhibit a stronger enhancement of mechanical properties compared to the
13
14 PNCs with high MWs. We ascribe the observed difference in mechanical reinforcement to an
15
16 increase in chain packing frustration in the interfacial layer with increase in MW. Our results
17
18 demonstrate that the PNC's mechanical moduli can be effectively tuned by changing only the chain
19
20 length, and that depending on molecular weight they can be either increased or decreased.
21
22
23
24
25

26 **Materials and Methods**

27
28 **Materials.** Poly(2-vinylpyridine) with different weight-average molecular weights (MW = 9.1,
29
30 35.9, 101.1, 216, and 404 kg/mol and polydispersity index below 1.2) were purchased from
31
32 Scientific Polymer Products Inc., and used as received. The silica nanoparticles (SiO_2 NPs) were
33
34 synthesized by a modified Stöber method⁴³ in ethanol with the final NP concentration of 16 mg/ml.
35
36 They were characterized by SAXS in ethanol at 0.7 vol% dilution. The scattered intensity revealed
37
38 a log-normal size distribution ($R_0 = 9.7$ nm, $\sigma = 17\%$), leading to an average nanoparticle radius
39
40 of 9.85 nm.
41
42
43

44 **Preparation of polymer nanocomposites.** The polymer and nanoparticles were mixed in ethanol
45
46 with proportions calculated to obtain a nominal silica content of 26 vol% in the final PNCs. Solvent
47
48 was evaporated during stirring at room temperature before further drying under vacuum at 403 K
49
50 for 48 hours in Teflon dishes. The real silica fractions in nanocomposites were obtained by
51
52 thermogravimetric analysis (TGA, Q50, TA Instruments, 20 K/min, under air) from the weight
53
54 loss between 403 K and 1073 K. The silica volume fraction, Φ_{NP} , was determined by mass
55
56
57
58
59
60

1
2
3
4
5
6 conservation using the density of the neat polymers measured by pycnometry and the silica density,
7
8 $\rho_{\text{NP}} = 2.406 \text{ g}\cdot\text{cm}^{-3}$.¹⁰ Differences in the obtained Φ_{NP} with respect to the expected values are due
9
10 to pipetting errors and precision of the weighting, and do not exceed 5%. The glass-transition
11
12 temperature, T_g , was determined using temperature-modulated differential scanning calorimetry
13
14 (Q2000, TA Instruments). Samples of about 10 mg were sealed in aluminum Tzero pans and
15
16 annealed at 433 K for 20 min. Then, they were measured at an average 2 K/min rate with
17
18 temperature modulation amplitude and period of ± 0.5 K and 60 s, respectively. T_g was defined as
19
20 the inflexion point temperature in the reversible heat flow upon heating.
21
22

23
24 **Small-angle X-ray scattering (SAXS)** experiments were performed with an in-house setup of the
25
26 Laboratoire Charles Coulomb, “Réseau X et gamma”, University of Montpellier, France. A high
27
28 brightness low power X-ray tube, coupled with aspheric multilayer optics (GeniX^{3D} from Xenocs)
29
30 was employed. It delivers an ultralow divergent beam (0.5 mrad). Scatterless slits were used to
31
32 give a clean 0.6 mm beam diameter with a flux of 35 Mphotons/s at the sample. We worked in a
33
34 transmission configuration and scattered intensity was measured by a 2D “Pilatus” pixel detector,
35
36 at a distance of 1900 mm from the sample. The scattering of the neat polymers, I_{Neat} , has been
37
38 measured independently in order to subtract the matrix contribution, $(1-\Phi_{\text{NP}}) I_{\text{Neat}}$, for each PNC
39
40 sample.
41
42

43
44 **Broadband dielectric spectroscopy (BDS).** Dielectric spectra were measured using disk-shaped
45
46 samples with a diameter of 20 mm. All samples have been hot pressed (423 K) to reach a typical
47
48 thickness of 0.15 mm, prior to drying under vacuum at 393 K for 3 days. Thin films were then
49
50 placed between gold plated electrodes forming a capacitor. For pure matrices, a ring of Teflon
51
52 (inner diameter of 16 mm, thickness 0.14 mm) was used as a spacer to prevent possible short-
53
54 circuits due to polymer flow. A broadband high-resolution dielectric spectrometer (Novocontrol
55
56
57
58
59
60

1
2
3
4
5
6 Alpha) was used to measure the complex dielectric permittivity, $\epsilon^*(\omega) = \epsilon'(\omega) - i \epsilon''(\omega)$, in the
7
8 frequency range from 10^{-2} to 10^7 Hz ($\omega = 2\pi f$). Before measurement each sample was annealed
9
10 for 1 h at 433 K in the BDS cryostat (under nitrogen atmosphere). Then isothermal frequency
11
12 measurements have been performed from 433 K down to 103 K, with temperature stability better
13
14 than 0.1 K. Then, the spectra were measured again at 293 K and 433 K in order to check the
15
16 reproducibility of our measurements. Accurate estimates of the volume fraction of the interfacial
17
18 layer require accurate measurements of the dielectric spectra in absolute values. To achieve that,
19
20 and to get rid of possible artefacts coming from (i) different surface states of the samples and (ii)
21
22 thickness variation due to temperature change, the complex permittivities have been normalized
23
24 using spectra measured at the lowest measurable temperature, $T = 103$ K. The real part of the
25
26 permittivity at such a low temperature corresponds to the dielectric constant, ϵ_∞ , which relates to
27
28 the refractive index. Considering that the latter depends on the molecular weight of the polymer
29
30 only at small values (typically below a few thousand),⁴⁴ we used an MW-independent value of ϵ_∞ .
31
32 In practice, the $\epsilon'(103 \text{ K})$ for the neat polymers have been rescaled to 3.05 using measurements on
33
34 the 36k-matrix. For PNCs, ϵ_∞ was calculated using a two-component model⁴⁵ that included silica
35
36 volume fraction, as well as taking $\epsilon_\infty = 3.05$ and 3.9 ⁴² for the polymer and silica permittivity
37
38 values, respectively (see SI for details). PNC data at 103 K were rescaled to this theoretical value,
39
40 and then the permittivity data at all other temperatures were rescaled by the same value estimated
41
42 at $T = 103$ K.
43
44
45
46
47
48

49 **Density measurements.** All samples were dried in the oven for at least 12 hours at 393 K before
50
51 density measurement. Density was measured at room temperature on Pycnometer AccuPyc II 1340
52
53 in helium. Each sample was measured at least seven times and the average value is presented in
54
55 Table 1. The standard deviation was found to be on the order of 1%.
56
57
58
59
60

1
2
3
4
5
6 **Brillouin light scattering (BLS).** Bubble-free polymer nanocomposite disks with a diameter of
7
8 10 mm and a thickness of 1 mm were first prepared and sandwiched by two sapphire glass windows
9
10 at 393 K and stored at this temperature in an oven under vacuum. The temperature was then
11
12 decreased to ambient very slowly using a cooling rate of about 0.2 K/min. All BLS measurements
13
14 were conducted in a symmetric scattering geometry at a 90 degree scattering angle using a solid
15
16 state laser (Verdi, $\lambda_{\text{laser}} = 532 \text{ nm}$).³⁹ The power of the incident laser beam was $\sim 5 \text{ mW}$. The
17
18 advantage of the symmetric scattering geometry is the compensation of the refractive index,⁴⁶
19
20 which provides an estimate of the sound velocity from the Brillouin peak frequency without
21
22 knowledge of the materials refractive index. Both VV and VH polarizations were utilized to
23
24 capture the longitudinal (VV and VH) and transverse modes (VH). All the measurements were
25
26 performed at room temperature with mirror distances in the tandem Fabry-Pérot interferometer
27
28 fixed to 7 mm for VV and 15 mm for VH polarizations, which covers the frequency range between
29
30 2 GHz and 21 GHz with a resolution of 0.04 GHz. The experimental error bar for the longitudinal
31
32 (V_L) and transverse (V_T) sound velocities did not exceed 0.2%.

41 **Results and Discussion**

42
43 Table 1 presents the characterization results of neat P2VP and silica-filled P2VP nanocomposites
44
45 (similar loadings) with different polymer molecular weights from 9 to 404 kg/mol. The T_g of the
46
47 PNCs is found to increase by $\sim 1.5 - 5 \text{ K}$ relative to the pure matrices (see SI for an illustration of
48
49 the trend in T_g and density).

Table 1. Characteristics of P2VP matrices and PNCs: sample name, silica concentration from TGA, glass-transition temperature from TMDSC and BDS, longitudinal (V_L) and transverse (V_T) sound velocities from BLS, bulk (K) and shear (G) moduli.

Sample name	Φ_{NP} [vol%]	T_g (TMDSC) [K]	T_g (BDS) [K]	Density [kg/m ³]	V_L [m/s]	V_T [m/s]	K [GPa]	G [GPa]
Neat-9k	0	364.3	357.9	1129	2652	1355	5.18±0.07	2.07±0.02
Neat-36k	0	373.1	366.1	1194	2616	1325	5.38±0.07	2.10±0.02
Neat-101k	0	376.6	369.3	1211	2606	1325	5.39±0.07	2.12±0.02
Neat-216k	0	377.1	368.5	1222	2608	1330	5.43±0.09	2.16±0.04
Neat-404k	0	376.8	369.2	1224	2605	1328	5.42±0.07	2.16±0.02
PNC-9k	26.3	369.6	365.0	1470	2899	1581	7.46±0.11	3.67±0.03
PNC-36k	25.0	375.5	370.7	1483	2955	1625	7.73±0.12	3.92±0.03
PNC-101k	26.3	378.5	373.1	1513	2943	1630	7.74±0.12	4.02±0.03
PNC-216k	27.3	378.5	372.1	1494	2936	1617	7.67±0.12	3.91±0.03
PNC-404k	26.1	378.2	372.6	1446	2924	1616	7.32±0.11	3.77±0.03

SAXS was used to analyze the nanoparticle dispersion in PNCs, where the scattered intensities were compared to form factor scattering (Figure 1a). All spectra show a well-defined repulsive interaction peak at intermediate q , corresponding to a dominant distance in the nanoparticle dispersion. The observed differences at low q may result from slight differences in the interactions and large-scale distribution of the filler particles in the matrix. It may for instance be caused by impurities. The local structure on the length scale of interest, i.e. the first layers of neighbors between particles as evidenced by the structure factor peak, turns out to be only marginally affected. The position of the peak, q_{NP} , is related to the typical center-to-center interparticle distance, $d = 2\pi/q_{NP}$, from which the average surface-to-surface interparticle spacing can be obtained, $IPS = d - 2R_{NP}$. The IPS values estimated from SAXS are reported in Figure 1b as $2R_g/IPS$, where R_g is the radius of gyration of the chain. They are in agreement with the theoretical estimates for IPS based on either a cubic or random⁴⁷ packing of nanoparticles in the sample, and

the NP volume fraction (Table 1). This result clearly indicates that nanoparticles are uniformly distributed in all PNCs studied here. The final organization of the nanoparticles in the PNC is set during the drying process when only part of the solvent has evaporated.⁴⁸ This step leads to a strong increase of the matrix viscosity inducing the freezing of the NP dispersion. As previously observed,⁴⁹ the choice of the polymer solvent (here ethanol) is crucial as it controls the formation of an adsorbed polymer layer onto the nanoparticles in suspension. Such a bound layer, whose thickness was found to be of the order of the polymer R_g in similar P2VP-silica PNCs,⁵⁰ provides steric stabilization and prevents NP agglomeration that would result from opposite forces like depletion attraction. We emphasize that it is not possible to describe the apparent PNC structure factor using only polydisperse hard-spheres interactions, which indicates the existence of additional repulsive long-range interactions between nanoparticles. The latter are most probably of electrostatic origin resulting from the presence of stabilizing charges on the silica surface.⁴⁸

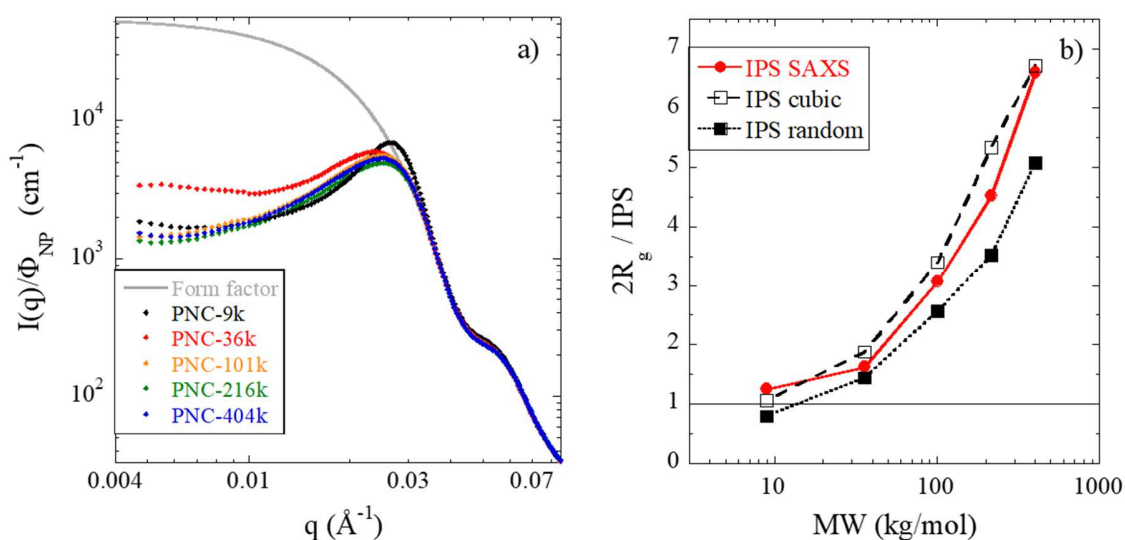


Figure 1. a) Reduced representation of the scattered intensity for a series of P2VP/silica nanocomposites with different molecular weights from 9 to 404 kg/mol and same silica content ($\Phi_{NP} \approx 26$ vol%). The NP form factor normalized to PNC scattering is represented by a continuous line. b) Ratio of P2VP chain size ($2R_g$) and different estimations of the interparticle spacing as a function of molecular weight.

1
2
3
4
5
6
7 Figure 2 presents the BLS spectra with the longitudinal modes (LM) in the main figure, and
8 transverse modes (TM) in the inset, for selected nanocomposites at similar loadings and a pure
9 polymer matrix for comparison. The BLS data of all measured samples (PNCs and neat polymers)
10 are presented in the SI. A clear shift towards high frequency is observed for both the LM and TM
11 of PNCs, indicating a more rigid medium with higher modulus relative to the neat polymer. To
12 extract the longitudinal and transverse sound frequencies, we fit our data to the damped harmonic
13 oscillator model, where we determined frequency of the peak positions ($\nu_{L,T}$). Using the
14 frequencies of the BLS peaks, we estimate the longitudinal and transverse sound velocities (Table
15 1) using the linear dispersion relationship for acoustic modes: $V_{L,T} = 2\pi\nu_{L,T} / Q$, where
16 $Q = 2\pi\sqrt{2} / \lambda_{laser}$ (this equation is valid for symmetric scattering at 90°). The shear ($G = \rho V_T^2$)
17 and longitudinal moduli ($M = \rho V_L^2$) are used to calculate the bulk modulus ($K = M - 4/3G$) by
18 using the mass density measured by pycnometry.⁵¹ The obtained densities and microscopic
19 mechanical moduli for the PNCs and neat polymers are reported in Table 1, and Figure 3a presents
20 the evolution of the PNC moduli K_{PNC} and G_{PNC} with the polymer molecular weight.
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

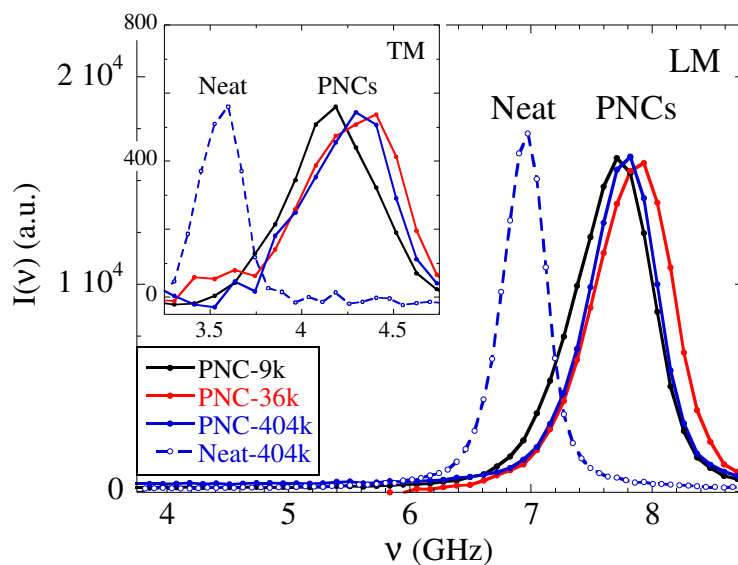


Figure 2. A representative plot of the longitudinal mode (LM) from Brillouin light scattering of neat P2VP (MW = 404 kg/mol) and selected P2VP/silica nanocomposites (PNCs, $\Phi_{NP} \approx 26$ vol%) with MW = 9, 36, and 404 kg/mol. Inset: transverse mode (TM).

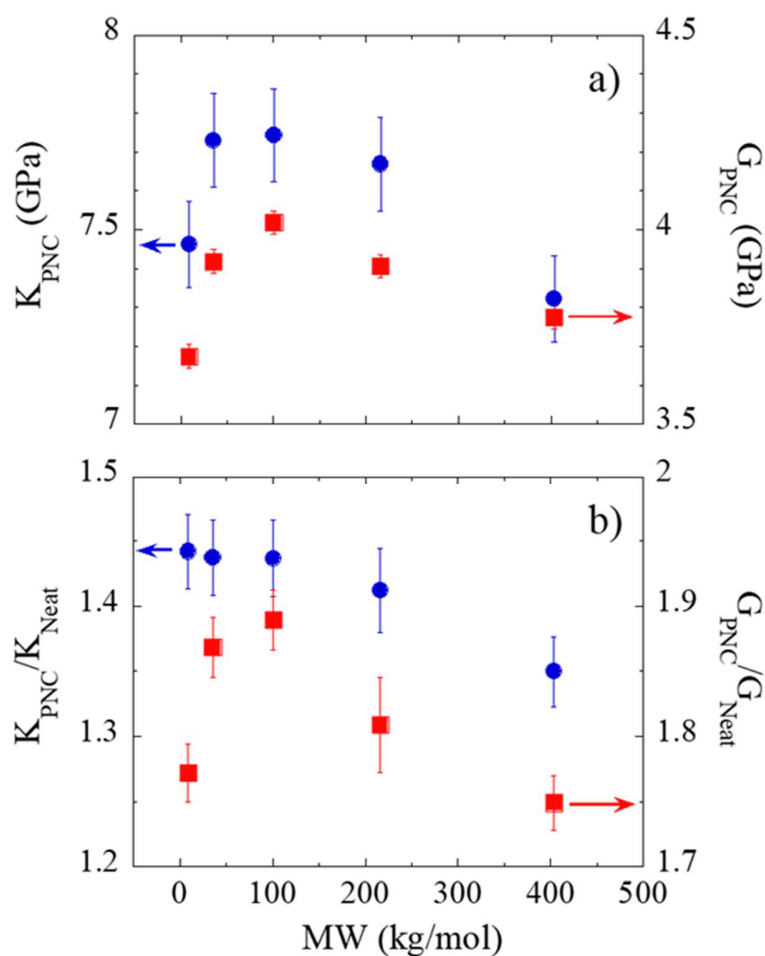


Figure 3. **a)** Bulk (K) and shear (G) moduli of P2VP/silica nanocomposites with different molecular weights. **b)** Normalization of the PNC moduli on the corresponding moduli of pure polymers with the same MW.

Both PNC moduli exhibit a non-monotonic dependence on MW (Fig. 3): initial increase with MW up to 100 kg/mol, followed by a decrease for higher MWs. To understand these data, we normalized them to the mechanical moduli of the neat polymers (Figure 3b). The non-monotonic trend remains, and it cannot be ascribed to nanoparticle aggregation, which was excluded by the SAXS results. To gain deeper insight into the mechanism of this non-monotonic behavior, a detailed analysis of the mechanical properties in the interfacial polymer layer surrounding the nanoparticles is required. The presence of an interfacial layer caused by the physical adsorption of

1
2
3
4
5
6 the polymer on the NP surface in P2VP-silica nanocomposites has been confirmed in previous
7
8 studies reported in literature.^{39, 52-53} To determine the individual contribution of this layer to the
9
10 mechanical properties of PNCs, we use the interfacial layer model (ILM) approach developed to
11
12 describe both mechanical and dielectric properties of heterogeneous systems.^{36, 54} Previous BLS
13
14 studies on P2VP³⁹ and poly(vinyl acetate) (PVAc)¹⁰ nanocomposites at different silica loadings
15
16 have demonstrated that ILM provides a much more accurate description of the mechanical
17
18 properties of PNCs than other existing models. The validity of ILM was also confirmed by a finite
19
20 element analysis in ref¹⁰. In order to apply the ILM model to the BLS data, it is first required to
21
22 determine the volume fraction of the interfacial region, which can be independently obtained using
23
24 broadband dielectric spectroscopy as detailed in the following part.
25
26
27
28
29

30 Comparisons between the dielectric loss spectra of selected nanocomposites and their
31
32 corresponding pure matrices are shown in Figure 4. Comparisons for all other MWs are presented
33
34 in SI. The PNC spectra display a shift of the main relaxation peak associated with the segmental
35
36 (α -) relaxation towards low frequencies, a reduction of its amplitude, and a significant broadening
37
38 in the peak shape. The low-frequency broadening of the α -relaxation reveals the interfacial layer
39
40 contribution, which has slower segmental dynamics than that of the bulk, as previously observed
41
42 in nanocomposites with attractive polymer-filler interaction.^{26, 55-56}
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

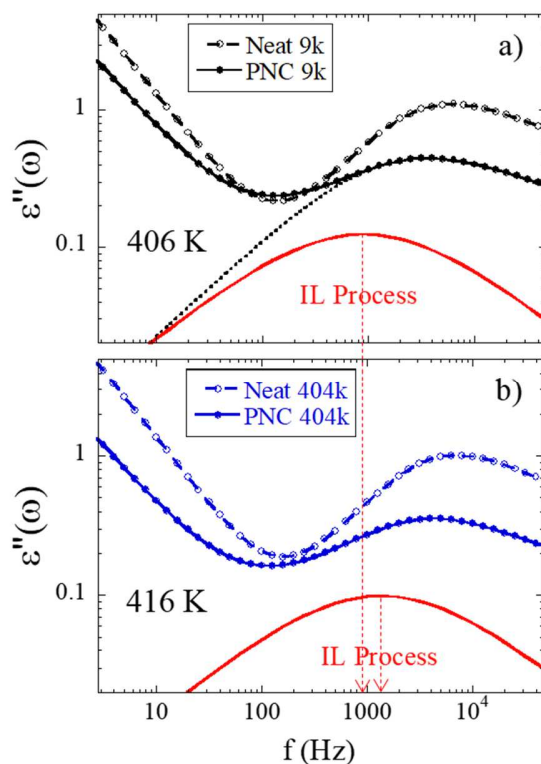


Figure 4. Comparison of the dielectric loss spectra, $\epsilon''(\omega)$, of the pure polymer matrix (empty circles) and PNC (plain circles) with MW = 9 kg/mol (a) and 404 kg/mol (b) both at $1.1T_g$ (T_g of the nanocomposite). The response from the interfacial layer process (red line) is shown for the nanocomposite samples. Arrows indicate the time scale $\tau_{\max}=1/(2\pi f_{\max})$ of this process. The dotted line for the PNC-9k in (a) presents a fit of the apparent peak maximum by a single HN function.

To describe the dielectric response of the interfacial layer, we use ILM.⁵⁴ In this model, we approximate the dielectric function of the interfacial layer by a (symmetric) Cole-Cole function, whereas the polymer bulk contribution was described by a Havriliak–Negami (HN) function⁵⁷ having the same spectral shape parameters and time scale as the dielectric function of the neat polymer. We emphasize that the ILM does not simply add these two contributions, but has a more complex form that explicitly takes into account interference terms in the dielectric response of heterogeneous systems (see ref⁵⁵ for details). The ILM analysis clearly separates the interfacial layer and bulk-like polymer contributions to the dielectric spectra (see, e.g., data for PNC-9k, and

1
2
3
4
5
6 PNC-404K in Figure 4). This analysis provides estimates of the characteristic relaxation time in
7
8 the interfacial layer (using the peak position) and the volume fraction of the interfacial layer from
9
10 the decrease in the amplitude of the bulk-like contribution. Figure 5a presents the temperature
11
12 dependence of the relaxation times of the interfacial layer in PNCs with two MWs, τ_{IL} , and of the
13
14 corresponding pure matrices, τ_{neat} . One can see that the interfacial layer process is significantly
15
16 slower than the dynamics of the bulk polymer and, more importantly, that the amplitude of this
17
18 slowing down depends on the polymer molecular weight. The evolution of the segmental dynamics
19
20 of the interfacial layer relative to the bulk, τ_{IL}/τ_{neat} , as a function of molecular weight is shown in
21
22 the inset of Figure 5a for a selected temperature, $T = 1.1 T_g$ (T_g of PNC). We chose this temperature
23
24 because it is the closest temperature to T_g where the interfacial layer relaxation process is still
25
26 within the experimental frequency window of BDS. Interestingly, stronger slowing down of the
27
28 interfacial dynamics is obtained for the lower molecular weight, and then it decreases
29
30 monotonously. The interfacial dynamics for PNC-9k is seven times slower comparing to the neat
31
32 polymer, while it is only five times slower in PNC-404k. Such results agree with our earlier results
33
34 on MW dependence in PVAc/silica nanocomposites.⁴² To verify that our results are not related to
35
36 any non-equilibrium issues, we annealed the highest MW PNC (where we expect the longest
37
38 equilibration times) at $T_g + 50$ K for an additional 15 days, which corresponds to about $10^{12} \tau_\alpha$.
39
40 Such an extremely long annealing did not produce any detectable changes in the segmental
41
42 relaxation spectra (Fig. S5), indicating that the samples are either at equilibrium or are trapped in
43
44 a very deep metastable state and are as close to equilibrium as experimentally possible. This was
45
46 also confirmed by measuring spectra twice at two selected temperatures using different path-ways
47
48 (see Materials and Methods section and details in SI). The spectra perfectly overlap demonstrating
49
50 that our BDS results are independent of the cooling protocol. Finally, one may note that a strong
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6 reduction of the physical aging rate has been reported in PNCs with attractive interactions at the
7
8 interface.⁵⁸⁻⁵⁹
9

10
11
12 To evaluate the overall segmental dynamics in nanocomposites, the apparent peak maximum in
13 the dielectric spectra is fitted with a single HN function over a restricted frequency range (Figure
14 4a), i.e., without any decomposition on interfacial layer and bulk contributions in this case. The
15 corresponding time scales are included in Figure 5a. At high temperatures, the segmental
16 relaxation times of the bulk polymer and the main PNC process tend to converge for both MWs.
17 As the temperature approaches T_g ($\tau_\alpha = 100$ s), the slowing down of the main peak in the PNC
18 relative to the pure matrix is stronger in PNC-9k than in PNC-404k. Such an observation indicates
19 that the behavior of the T_g -shift strongly depends on the molecular weight in these PNCs. The
20 dynamic glass-transition temperature can be determined by fitting the temperature dependence of
21 the segmental relaxation times (main process for PNCs) to the Vogel-Fulcher-Tammann (VFT)
22 equation (Figure 5a), and extrapolating to the temperature at which $\tau_\alpha = 100$ s. The obtained values
23 are in good agreement with the calorimetric T_g (see Table 1 and Figure 5b). For the lowest
24 molecular weight, the difference in T_g between the nanocomposite and the neat polymer is the
25 highest (5.3 K by TMDSC), and this difference decreases with the increase of molecular weight.
26 It reaches the value of only 1.4 K for MW = 404 kg/mol. This result further confirms that the
27 dynamics of the interfacial layer process has a larger slowing down in low-MW PNCs comparing
28 to high-MW ones.
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

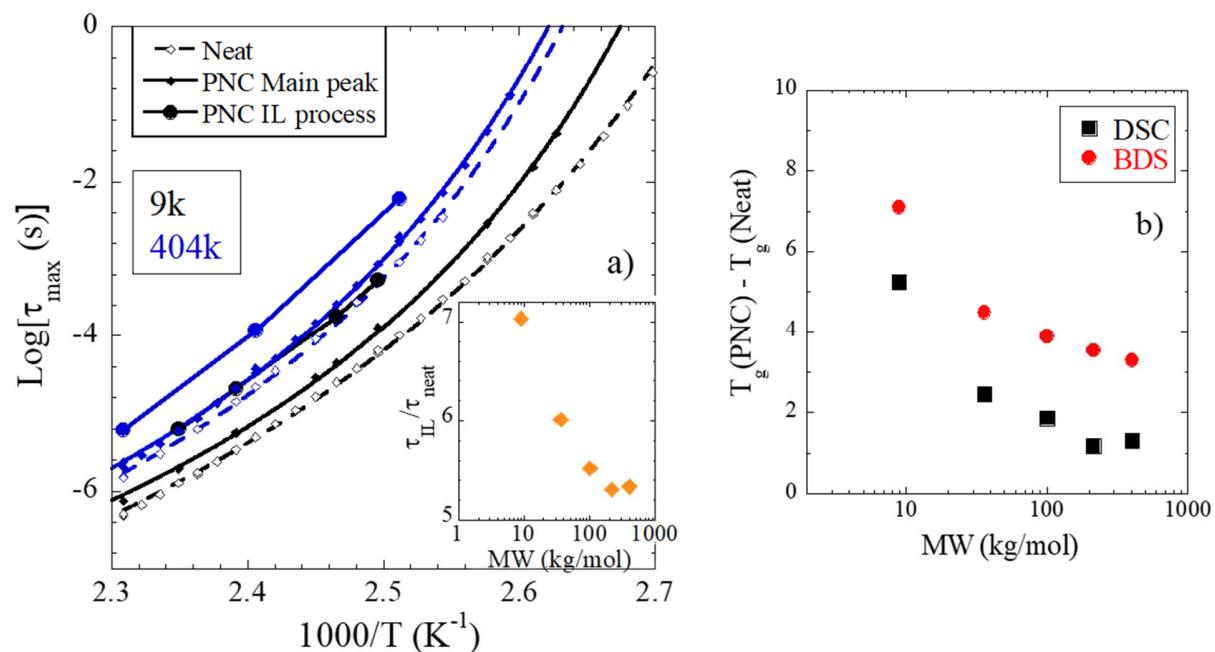


Figure 5. a) Temperature dependence of the interfacial segmental relaxation times, τ_{IL} (filled circles), for P2VP/silica nanocomposites with MW = 404 kg/mol (blue) and 9 kg/mol (black), averaged PNC dynamics (filled diamonds), and bulk-like dynamics, τ_{neat} (empty diamonds), with their fits by the Vogel-Fulcher-Tammann equation. Inset: Ratio of τ_{IL} to τ_{neat} corresponding to the interfacial layer slowing down at 1.1Tg. **b)** Change in T_g of PNCs with respect to corresponding neat polymers as a function of MW.

We now turn to the interfacial layer volume fraction, Φ_{IL} , obtained from the ILM analysis. One can see in Figure 6 that the interfacial layer fraction with slowed-down dynamics does not show any significant MW dependence, and takes an average value of 47 vol%. It means that there is only about 27 vol% of bulk-like polymer left in the interstitial space between nanoparticles, which gives rise to a bulk dielectric signal in all PNCs (another 26 vol% is occupied by silica). The estimation of the interfacial layer thickness from Φ_{IL} is straightforward using simple geometric considerations with a cubic arrangement of nanoparticles, and taking into account the overlapping volume between surrounding interfacial layers (see SI for details). We find an average thickness

of about 4.3 nm (Figure 6). It means that, in P2VP-silica PNCs, both the silica loading (see ref ⁵²) and MW do not play a significant role on the interfacial layer thickness.

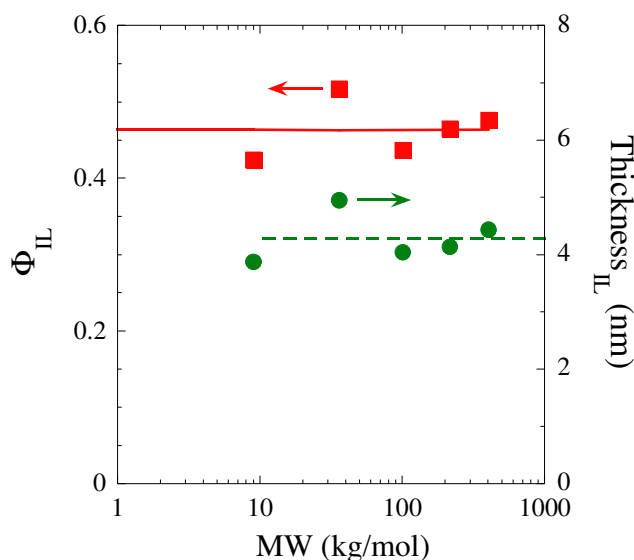


Figure 6. Volume fraction and estimated thickness of interfacial layer surrounding the silica nanoparticles in P2VP nanocomposites with similar loadings ($\Phi_{NP} \approx 26$ vol%) and different MWs. Lines show the average values.

Using the so obtained volume fraction, it is then possible to apply the ILM model and calculate the bulk and shear moduli of the interfacial layer from the BLS results (Table 1 and Figure 3). ILM predicts the elastic response of the nanocomposites as ³⁶

$$K_{PNC} = \frac{K_{NP} \Phi_{NP} + K_{IL} \Phi_{IL} R + K_{Neat} \Phi_{Neat} S}{\Phi_{NP} + \Phi_{IL} R + \Phi_{Neat} S} \quad (1)$$

$$\text{with } S = \frac{(3K_{NP} + 4G_{NP})(3K_{IL} + 4G_{Neat}) - 12d(K_{IL} - K_{NP})(G_{IL} - G_{Neat})}{\Phi_{NP} + \Phi_{IL} R + \Phi_{Neat} S}, \quad R = \frac{3K_{NP} + 4G_{IL}}{3K_{IL} + 4G_{IL}} \quad \text{and} \quad d = \frac{\Phi_{NP}}{\Phi_{NP} + \Phi_{IL}}$$

$\Phi_{IL} + \Phi_{NP} + \Phi_{Neat} = 1$, where Φ is the volume fraction and the sub-indices Neat, NP, IL, and PNC stand for pure polymer (bulk), silica nanoparticles, interfacial layer, and nanocomposite, respectively. K_{IL} is the bulk modulus and G_{IL} the shear modulus of the interfacial layer. Further

1
 2
 3
 4
 5
 6 details on the ILM calculation can be found in refs ^{10,36}. In eq 1, the bulk and shear moduli of the
 7
 8 nanoparticles are fixed to $K_{NP} = 35.12$ GPa and $G_{NP} = 30.06$ GPa, which are calculated by assuming
 9
 10 the sound velocity of the NP is the same as in fused silica. ⁶⁰ For all PNC samples, we use the
 11
 12 average value of Φ_{IL} (47 vol%, see Figure 6), which was obtained at a selected temperature $T =$
 13
 14 $1.1T_g$ (T_g of PNC) as the closest to the glassy state in our experiments. The mechanical properties
 15
 16 of the interfacial layer calculated using eq 1 are presented in Figure 7a. The results reveal a
 17
 18 significant increase in the glassy moduli of interfacial layer in the case of PNC-9k and PNC-36k,
 19
 20 while a much weaker increase in shear modulus and even a drop in the bulk modulus are observed
 21
 22 for the interfacial layer in PNC-216k and PNC-404k.
 23
 24
 25
 26
 27
 28
 29
 30
 31
 32
 33
 34
 35
 36
 37
 38
 39
 40
 41
 42
 43
 44
 45
 46
 47
 48
 49
 50
 51
 52
 53
 54
 55
 56
 57
 58
 59
 60

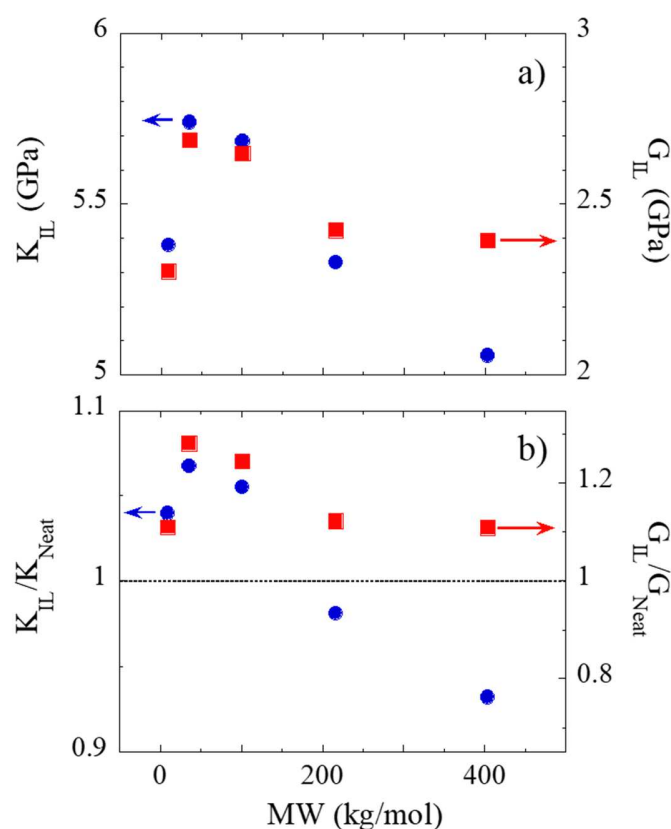


Figure 7. a) Bulk modulus, K_{IL} , and shear modulus, G_{IL} , of interfacial layer in P2VP/silica nanocomposites ($\Phi_{NP} \approx 26$ vol%) from ILM calculations using $\Phi_{IL} = 47$ vol%. **b)** Ratio of the mechanical moduli of interfacial layer to the moduli of the corresponding matrix (neat).

The differences observed between the interfacial layer moduli for PNCs with different molecular weights are likely the result of the difference in polymer rearrangement in the interface promoted by different MW of the matrix. Here, molecular features like chain packing, stretching of the polymer near the NP surface,⁴² and polymer bridging play an important role. For instance, any difference in chain packing is expected to induce some changes in macroscopic density. To confirm this conjecture, we estimate the average density of the polymer matrix, $\rho_{\text{Matrix}}^{\text{PNC}}$, in the PNCs (Figure 8). The ratio of this quantity to the density of the neat polymer of same mass is shown in Figure 8a, where a clear evolution with molecular weight can be seen. The relative average density of the matrix in PNC is slightly higher than one for PNC-9k, as expected due to the attractive polymer-filler interaction, but then it decreases below one for higher molecular weights. This confirms that packing of the chains in nanocomposites depends strongly on the chain length. A similar evolution of $\rho_{\text{matrix}}^{\text{PNC}} / \rho_{\text{Neat}}$ with MW was reported and discussed in ref⁴² for PVAc/silica PNCs, suggesting some general behavior of PNCs with attractive interactions.

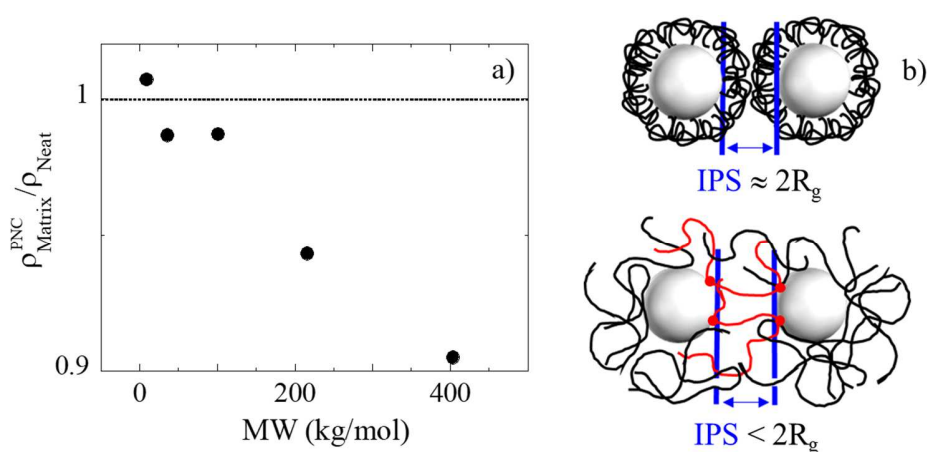


Figure 8. a) Ratio between average density of the matrix in P2VP/silica nanocomposite, $\rho_{\text{matrix}}^{\text{PNC}}$, and density of the pure polymer, ρ_{Neat} , for different molecular weights. $\rho_{\text{matrix}}^{\text{PNC}} = \frac{\rho_{\text{PNC}} - \rho_{\text{NP}} \Phi_{\text{NP}}}{1 - \Phi_{\text{NP}}}$, where ρ_{PNC} and ρ_{NP} are the densities of PNC and silica NPs, respectively. b) Sketch of the chains confined between nanoparticles for low and high MW cases.

1
2
3
4
5
6 The density evolution can explain the decrease in mechanical properties of higher-MW PNCs,
7
8 which is especially pronounced for PNC-216k and PNC-404k (Figure 7). The main idea here is
9
10 that polymer chains adsorbed onto the silica NPs can experience different conformations, which
11
12 are affected by many parameters, including MW and IPS. According to theory and simulations,
13
14 adsorbed chains can form loops, trains, and tails near the NP surface.^{40, 61} When the distance
15
16 between NP surfaces becomes smaller than the size of the chain ($\sim 2 R_g$), large polymer loops in
17
18 high-MW PNCs are strongly confined between nanoparticles.^{26, 42} This effect induces strong
19
20 repulsive chain-chain interactions in the interfacial region, where the loops repel each other,
21
22 leading to loose polymer packing and a lower density than in the bulk. However, in the case of
23
24 low-MW PNCs, the chains are able to pack better because of their small size and the significant
25
26 amount of free (non-adsorbed) chains. They may therefore arrange their conformation leading to
27
28 a dense packing. This is in agreement with the evolution of the interfacial layer properties, which
29
30 displays a stronger slowing down at low MW (inset of Figure 5a), while the volume fraction of
31
32 interphase does not vary much (Figure 6). This behavior means that the dynamical changes
33
34 observed in Figure 5 are not a function of how much polymer is impacted at the interface, but the
35
36 result of different packing in the interfacial region. Since the density directly correlates with
37
38 mechanical properties, the decrease in density ultimately leads to a decrease in mechanical moduli.
39
40 However, density and chain packing alone are not sufficient to explain the maximum in bulk and
41
42 shear moduli of interfacial layer obtained for PNC-36k. In this nanocomposite, the density is lower
43
44 than the density of the pure polymer, while mechanical properties are maximal. Such behavior
45
46 suggests the presence of other mechanisms of mechanical enhancement.
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6 Bridging⁶² of polymer chains between nanoparticles has been reported in literature for PNCs in
7
8 glassy¹⁰ and rubbery^{8-9, 63} states. This mechanism is actively used in particle flocculation.⁶⁴ We
9
10 believe that in our case, bridging is promoted by the high concentration of nanoparticles since the
11
12 interparticle spacing is equal or smaller than $2 R_g$ of the polymer (Figure 1b). If polymer chains
13
14 are adsorbed simultaneously on more than one particle, it can be expected that IPS displays a
15
16 broader distribution, whereas absence of bridging may induce purely repulsive interactions leading
17
18 to a narrower distribution of the interparticle distances. It is interesting to note that in PNC-9k,
19
20 where the IPS is about $2 R_g$ of the polymer, the distribution of IPS deduced from the width of the
21
22 repulsive interaction peak in SAXS is indeed narrower than in all other MWs (Figure 1a). This
23
24 may suggest that bridging is unlikely for the low-MW PNC. The interaction peak becomes broader
25
26 already in PNC-36k, and the most probable interparticle distance slightly decreases with increase
27
28 of MW (IPS = 6.4 and 5.3 nm for MW = 36 and 404 kg/mol, respectively). This suggests initiation
29
30 and possible progression of the bridges with decrease in IPS, as predicted by De Gennes for the
31
32 case of flat surfaces.^{9, 62} Chain bridging between nanoparticles, on one hand, leads to an
33
34 improvement of the mechanical properties;¹⁰ on the other hand, it facilitates a significant
35
36 frustration in chain packing (see Figure 8b) that causes the drop in density and reduction of
37
38 mechanical properties. Thus, the combined evolution of density and bridging may explain the non-
39
40 monotonic behavior of mechanical properties with MW.
41
42
43
44
45
46
47

48
49 Another possible mechanism of mechanical enhancement is related to chain stretching in the
50
51 interfacial layer. This effect has been proposed in theoretical works,^{61, 65-66} where it was
52
53 demonstrated that polymer adsorbed onto a solid wall will adopt a stretched conformation. It was
54
55 also demonstrated experimentally for polymer brushes covalently grafted on a flat surface⁶⁷ or
56
57
58
59
60

1
2
3
4
5
6 grafted on spherical nanoparticles.⁶⁸⁻⁶⁹ However, the degree of stretching for nanocomposites
7
8 varies with the chain length. For instance, using self-consistent field theory calculations in PNCs,
9
10 it was shown that stretching decreases with the MW increase.⁷⁰ Furthermore, it has also been
11
12 shown that chain stretching leads to enhancement of mechanical properties (along the stretching
13
14 direction).⁷¹⁻⁷² In our case, this would mean that short and intermediate chains are stretched
15
16 stronger than longer chains, which might be the reason for improvement in mechanical properties
17
18 in these PNCs. Unfortunately, we do not have any experimental measure of chain stretching to
19
20 support this idea, and it is difficult to evaluate whether stretching, bridging, or some other effects
21
22 dominate the enhancement of mechanical properties. However, the presented experimental results
23
24 revealed the existence of optimal conditions for achieving mechanical reinforcement that are
25
26 realized in PNC-36k in our case.
27
28
29
30
31

32
33 Although we do not have any direct evidence of chain stretching and bridging in PNCs (more
34
35 theoretical and experimental studies are on the way to address these points), some indirect evidence
36
37 exists in our studies. We found that the interfacial layer bulk modulus and shear modulus have a
38
39 different behavior. The interfacial layer modulus G_{IL} is always above the shear modulus of the
40
41 neat polymers (Figure 7b), while the bulk modulus K_{IL} is below that of the neat polymer at high
42
43 MW. In general, bulk modulus relates to the inverse of material's compressibility and is more
44
45 sensitive to the density, while shear modulus is a deformation that is more sensitive to the
46
47 anisotropic conformation of the polymer chains and hence more affected by chain stretching and
48
49 bridging. Furthermore, we also found that the segmental dynamics of the interfacial layer are
50
51 slower than the bulk segmental dynamics in all PNCs, but the observed slowing down is more
52
53 pronounced at low MW. This finding is in line with theoretical works predicting a slowing down
54
55
56
57
58
59
60

1
2
3
4
5
6 of segmental dynamics^{70, 73} in systems with more stretched polymer chains. Slowing down of the
7
8 dynamics in our nanocomposites has a different magnitude with MW, further highlighting a
9
10 complex interplay of chain stretching, packing (density), and bridging.
11
12
13
14

15 **Conclusions**

16
17 In summary, we presented measurements of mechanical properties in glassy P2VP/silica
18
19 nanocomposites with different molecular weights and a single high NP loading (≈ 26 vol%). Our
20
21 results suggest that mechanical properties are strongly influenced by the MW of the polymer and
22
23 represent a complex interplay between chain packing, stretching, and bridging, which are acting
24
25 in opposite directions. Strong enhancement in the glassy mechanical properties is achieved at low
26
27 MW, with the maximum for PNC-36k, while further increase in MW results in a decrease of the
28
29 mechanical properties enhancement. Such a non-monotonic dependence results from a complex
30
31 interplay between chain packing and stretching in the interfacial polymer layer and formation of
32
33 inter-particle bridges. Using ILM, and the independently estimated thickness of the interfacial
34
35 layer, we estimated the glassy mechanical moduli in the interfacial region surrounding
36
37 nanoparticles. The interfacial region occupies about 64 %vol of the polymer matrix in the studied
38
39 PNCs. The mechanical moduli of the interfacial layer exhibit strong enhancement at low MW that
40
41 decreases at larger MW due to frustration in packing of chains strongly confined between
42
43 nanoparticles. In particular, the bulk modulus in the interfacial layer of high-MW PNCs appears
44
45 to be even lower than in the neat polymer. Our results also reveal that the slowing down of PNC
46
47 segmental dynamics and the shift in PNC T_g decrease with polymer MW, suggesting a common
48
49 structural origin controlling glassy moduli and structural relaxation in nanocomposites. We
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6 emphasize that the presented finding provides a clear guidance on how mechanical properties of
7
8 glassy PNCs can be tuned by changing only polymer molecular weight.
9

10
11
12 **Supporting Information:** Normalization of BDS data, characterization results, BLS data of all
13
14 materials tested, additional comparison of BDS spectra, annealing effect, estimation of the
15
16 overlapping volume between interfacial layers,
17
18

19
20
21 **Author Contributions:** All authors contributed to writing the manuscript and have given approval
22
23 to the final version of the manuscript.
24
25

26 27 28 **ACKNOWLEDGMENT**

29
30 This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy
31
32 Sciences, Materials Sciences and Engineering Division. ACG and JO are thankful for support by
33
34 the ANR NANODYN project, Grant ANR-14-CE22-0001-01 of the French Agence Nationale de
35
36 la Recherche. SAXS measurements by Philippe Dieudonné-George (L2C) are gratefully
37
38 acknowledged.
39
40

41 42 43 **ABBREVIATIONS**

44
45 P2VP, Poly(2-vinyl pyridine); PNCs, polymer nanocomposites; MW, molecular weight; ILM,
46
47 interfacial layer model; BDS, broadband dielectric spectroscopy; TMDSC, temperature-modulated
48
49 differential scanning calorimetry; SAXS, small-angle X-ray scattering; BLS, Brillouin light
50
51 scattering
52
53
54
55
56
57
58
59
60

REFERENCES

1. Suematsu, K.; Arimura, M.; Uchiyama, N.; Saita, S., Transparent BaTiO₃/PMMA Nanocomposite Films for Display Technologies: Facile Surface Modification Approach for BaTiO₃ Nanoparticles. *ACS Applied Nano Materials* **2018**, *1* (5), 2430-2437.
2. Mittal, V.; Kim, J. K.; Pal, K., *Recent Advances in Elastomeric Nanocomposites*. Springer-Verlag: Berlin Heidelberg, 2011.
3. 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* (15), 3321-3343.
4. Matteucci, S.; Kusuma, V. A.; Kelman, S. D.; Freeman, B. D., Gas Transport Properties of MgO Filled Poly(1-Trimethylsilyl-1-Propyne) Nanocomposites. *Polymer* **2008**, *49* (6), 1659-1675.
5. Chevigny, C.; Jouault, N.; Dalmas, F.; Boue, F.; Jestin, J., Tuning the Mechanical Properties in Model Nanocomposites: Influence of the Polymer-Filler Interfacial Interactions. *J. Polym. Sci., Part B: Polym. Phys.* **2011**, *49* (11), 781-791.
6. Mujtaba, A.; Keller, M.; Ilisch, S.; Radusch, H. J.; Beiner, M.; Thurn-Albrecht, T.; Saalwächter, K., Detection of Surface-Immobilized Components and Their Role in Viscoelastic Reinforcement of Rubber-Silica Nanocomposites. *ACS Macro Letters* **2014**, *3* (5), 481-485.
7. 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* (26), 9756-9762.

- 1
2
3
4
5
6 8. Papon, A.; Montes, H.; Lequeux, F.; Oberdisse, J.; Saalwächter, K.; Guy, L., Solid Particles
7
8 in an Elastomer Matrix: Impact of Colloid Dispersion and Polymer Mobility Modification on
9
10 the Mechanical Properties. *Soft Matter* **2012**, *8* (15), 4090-4096.
- 11
12 9. Chen, Q.; Gong, S.; Moll, J.; Zhao, D.; Kumar, S. K.; Colby, R. H., Mechanical Reinforcement
13
14 of Polymer Nanocomposites from Percolation of a Nanoparticle Network. *ACS Macro Letters*
15
16 **2015**, *4* (4), 398-402.
- 17
18 10. Cheng, S.; Bocharova, V.; Belianinov, A.; Xiong, S.; Kisliuk, A.; Somnath, S.; Holt, A. P.;
19
20 Ovchinnikova, O. S.; Jesse, S.; Martin, H.; Etampawala, T.; Dadmun, M.; Sokolov, A. P.,
21
22 Unraveling the Mechanism of Nanoscale Mechanical Reinforcement in Glassy Polymer
23
24 Nanocomposites. *Nano Letters* **2016**, *16* (6), 3630-3637.
- 25
26 11. Pryamitsyn, V.; Ganesan, V., Origins of Linear Viscoelastic Behavior of
27
28 Polymer–Nanoparticle Composites. *Macromolecules* **2006**, *39* (2), 844-856.
- 29
30 12. Hashemi, A.; Jouault, N.; Williams, G. A.; Zhao, D.; Cheng, K. J.; Kysar, J. W.; Guan, Z.;
31
32 Kumar, S. K., Enhanced Glassy State Mechanical Properties of Polymer Nanocomposites Via
33
34 Supramolecular Interactions. *Nano Letters* **2015**, *15* (8), 5465-5471.
- 35
36 13. Kim, H.; Abdala, A. A.; Macosko, C. W., Graphene/Polymer Nanocomposites.
37
38 *Macromolecules* **2010**, *43* (16), 6515-6530.
- 39
40 14. Su, S.; Jiang, D. D.; Wilkie, C. A., Methacrylate Modified Clays and Their Polystyrene and
41
42 Poly(Methyl Methacrylate) Nanocomposites. *Polymers for Advanced Technologies* **2004**, *15*
43
44 (5), 225-231.
- 45
46 15. Tao, R.; Simon, S. L., Bulk and Shear Rheology of Silica/Polystyrene Nanocomposite:
47
48 Reinforcement and Dynamics. *J. Polym. Sci. B Polym. Phys.* **2015**, *53* (9), 621-632.
- 49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4
5
6 16. Smallwood, H. M., Limiting Law of the Reinforcement of Rubber. *J Appl Phys* **1944**, *15*, 758-
7
8 766.
9
10
11 17. Guth, E., Theory of Filler Reinforcement. *J Appl Phys* **1945**, *16*, 20-25.
12
13 18. Einstein, A., Eine Neue Bestimmung Der Moleküldimensionen. *Annalen Der Physik* **1906**,
14
15 324 (2), 289-306.
16
17 19. Krishnamoorti, R.; Chatterjee, T., Carbon Nanotube-Based Poly(Ethylene Oxide)
18
19 Nanocomposites. In *Handbook of Polymer Nanocomposites. Processing, Performance and*
20
21 *Application: Volume B: Carbon Nanotube Based Polymer Composites*, Kar, K. K.; Pandey, J.
22
23 K.; Rana, S., Eds. Springer Berlin Heidelberg: Berlin, Heidelberg, 2015; pp 299-334.
24
25
26 20. Akcora, P.; Kumar, S. K.; Moll, J.; Lewis, S.; Schadler, L. S.; Li, Y.; Benicewicz, B. C.;
27
28 Sandy, A.; Narayanan, S.; Illavsky, J.; Thiyagarajan, P.; Colby, R. H.; Douglas, J. F., "Gel-
29
30 Like" Mechanical Reinforcement in Polymer Nanocomposite Melts. *Macromolecules* **2010**,
31
32 43 (2), 1003-1010.
33
34
35 21. Oberdisse, J., Aggregation of Colloidal Nanoparticles in Polymer Matrices. *Soft Matter* **2006**,
36
37 2 (1), 29-36.
38
39
40 22. Baeza, G. P.; Genix, A. C.; Degrandcourt, C.; Petitjean, L.; Gummel, J.; Couty, M.; Oberdisse,
41
42 J., Multiscale Filler Structure in Simplified Industrial Nanocomposite Silica/SBR Systems
43
44 Studied by SAXS and TEM. *Macromolecules* **2013**, *46* (1), 317-329.
45
46
47 23. Akcora, P.; Liu, H.; Kumar, S. K.; Moll, J.; Li, Y.; Benicewicz, B. C.; Schadler, L. S.; Acehan,
48
49 D.; Panagiotopoulos, A. Z.; Pryamitsyn, V.; Ganesan, V.; Ilavsky, J.; Thiyagarajan, P.; Colby,
50
51 R. H.; Douglas, J. F., Anisotropic Self-Assembly of Spherical Polymer-Grafted Nanoparticles.
52
53 *Nat Mater* **2009**, *8* (4), 354-359.
54
55
56
57
58
59
60

- 1
2
3
4
5
6 24. Maillard, D.; Kumar, S. K.; Fragneaud, B.; Kysar, J. W.; Rungta, A.; Benicewicz, B. C.; Deng,
7
8 H.; Brinson, L. C.; Douglas, J. F., Mechanical Properties of Thin Glassy Polymer Films Filled
9
10 with Spherical Polymer-Grafted Nanoparticles. *Nano Letters* **2012**, *12* (8), 3909-3914.
11
12 25. Kumar, S. K.; Jouault, N.; Benicewicz, B.; Neely, T., Nanocomposites with Polymer Grafted
13
14 Nanoparticles. *Macromolecules* **2013**, *46* (9), 3199-3214.
15
16 26. Cheng, S.; Carroll, B.; Bocharova, V.; Carrillo, J.-M.; Sumpter, B. G.; Sokolov, A. P., Focus:
17
18 Structure and Dynamics of the Interfacial Layer in Polymer Nanocomposites with Attractive
19
20 Interactions. *J. Chem. Phys.* **2017**, *146* (20), 203201.
21
22 27. Berriot, J.; Montes, H.; Lequeux, F.; Long, D.; Sotta, P., Gradient of Glass Transition
23
24 Temperature in Filled Elastomers. *Europhysics Letters* **2003**, *64* (1), 50-56.
25
26 28. Qu, M.; Deng, F.; Kalkhoran, S. M.; Gouldstone, A.; Robisson, A.; Van Vliet, K. J., Nanoscale
27
28 Visualization and Multiscale Mechanical Implications of Bound Rubber Interphases in
29
30 Rubber-Carbon Black Nanocomposites. *Soft Matter* **2011**, *7* (3), 1066-1077.
31
32 29. Cheng, X.; Putz, K. W.; Wood, C. D.; Brinson, L. C., Characterization of Local Elastic
33
34 Modulus in Confined Polymer Films Via Afm Indentation. *Macromolecular Rapid*
35
36 *Communications* **2015**, *36* (4), 391-397.
37
38 30. Xia, W.; Song, J.; Hsu, D. D.; Keten, S., Understanding the Interfacial Mechanical Response
39
40 of Nanoscale Polymer Thin Films Via Nanoindentation. *Macromolecules* **2016**, *49* (10), 3810-
41
42 3817.
43
44 31. VanLandingham, M. R.; Dagastine, R. R.; Eduljee, R. F.; McCullough, R. L.; Gillespie, J. W.,
45
46 Characterization of Nanoscale Property Variations in Polymer Composite Systems: 1.
47
48 Experimental Results. *Composites Part A: Applied Science and Manufacturing* **1999**, *30* (1),
49
50 75-83.
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4
5
6 32. Rouxel, D.; Thevenot, C.; Nguyen, V. S.; Vincent, B., Chapter 12 - Brillouin Spectroscopy of
7
8 Polymer Nanocomposites. In *Spectroscopy of Polymer Nanocomposites*, William Andrew
9
10 Publishing: 2016; pp 362-392.
11
12 33. Zhao, D.; Schneider, D.; Fytas, G.; Kumar, S. K., Controlling the Thermomechanical
13
14 Behavior of Nanoparticle/Polymer Films. *ACS Nano* **2014**, *8* (8), 8163-8173.
15
16 34. Still, T.; Sainidou, R.; Retsch, M.; Jonas, U.; Spahn, P.; Hellmann, G. P.; Fytas, G., The
17
18 “Music” of Core–Shell Spheres and Hollow Capsules: Influence of the Architecture on the
19
20 Mechanical Properties at the Nanoscale. *Nano Letters* **2008**, *8* (10), 3194-3199.
21
22 35. Smith, J. C., Correction and Extension of Van der Poel's Method for Calculating the Shear
23
24 Modulus of a Particulate Composite. *J. Res. Natl. Bur. Stand., Sect. A* **1974**, *78A* (3), 355-361.
25
26 36. Maurer, F. H. J. In *An Interlayer Model to Describe the Physical Properties of Particulate*
27
28 *Composites*, Dordrecht, Springer Netherlands: Dordrecht, 1990; pp 491-504.
29
30 37. Maurice, G.; Rouxel, D.; Vincent, B.; Hadji, R.; Schmitt, J. F.; Taghite, M. b.; Rahouadj, R.,
31
32 Investigation of Elastic Constants of Polymer/Nanoparticles Composites Using the Brillouin
33
34 Spectroscopy and the Mechanical Homogenization Modeling. *Polymer Engineering &*
35
36 *Science* **2013**, *53* (7), 1502-1511.
37
38 38. Voudouris, P.; Choi, J.; Gomopoulos, N.; Sainidou, R.; Dong, H.; Matyjaszewski, K.;
39
40 Bockstaller, M. R.; Fytas, G., Anisotropic Elasticity of Quasi-One-Component Polymer
41
42 Nanocomposites. *ACS Nano* **2011**, *5* (7), 5746-5754.
43
44 39. Holt, A. P.; Bocharova, V.; Cheng, S.; Kisliuk, A. M.; Ehlers, G.; Mamontov, E.; Novikov,
45
46 V. N.; Sokolov, A. P., Interplay between Local Dynamics and Mechanical Reinforcement in
47
48 Glassy Polymer Nanocomposites. *Physical Review Materials* **2017**, *1* (6), 062601.
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4
5
6 40. Scheutjens, J. M. H. M.; Fleer, G. J., Statistical Theory of the Adsorption of Interacting Chain
7
8 Molecules. 2. Train, Loop, and Tail Size Distribution. *The Journal of Physical Chemistry*
9
10 **1980**, *84* (2), 178-190.
11
12 41. Jouault, N.; Moll, J. F.; Meng, D.; Windsor, K.; Ramcharan, S.; Kearney, C.; Kumar, S. K.,
13
14 Bound Polymer Layer in Nanocomposites. *ACS Macro Letters* **2013**, *2* (5), 371-374.
15
16 42. Cheng, S. W.; Holt, A. P.; Wang, H. Q.; Fan, F.; Bocharova, V.; Martin, H.; Etampawala, T.;
17
18 White, B. T.; Saito, T.; Kang, N. G.; Dadmun, M. D.; Mays, J. W.; Sokolov, A. P., Unexpected
19
20 Molecular Weight Effect in Polymer Nanocomposites. *Physical Review Letters* **2016**, *116* (3).
21
22 43. Hidehiro, K.; Hisao, S.; Daisuke, K.; Genji, J., Densification of Alkoxide-Derived Fine Silica
23
24 Powder Compact by Ultra-High-Pressure Cold Isostatic Pressing. *Journal of the American*
25
26 *Ceramic Society* **1993**, *76* (1), 54-64.
27
28 44. Barrall, E. M.; Cantow, M. J. R.; Johnson, J. F., Variation of Refractive Index of Polystyrene
29
30 with Molecular Weight: Effect on the Determination of Molecular Weight Distributions.
31
32 *Journal of Applied Polymer Science* **1968**, *12* (6), 1373-1377.
33
34 45. Kremer, F.; Schönhals, A., *Broadband Dielectric Spectroscopy*. Springer-Verlag: Heidelberg,
35
36 2003.
37
38 46. Krüger, J. K.; Embs, J.; Brierley, J.; Jiménez, R. A., A New Brillouin Scattering Technique
39
40 for the Investigation of Acoustic and Opto-Acoustic Properties: Application to Polymers.
41
42 *Journal of Physics D: Applied Physics* **1998**, *31* (15), 1913.
43
44 47. Hao, T.; Riman, R. E., Calculation of Interparticle Spacing in Colloidal Systems. *J. Colloid*
45
46 *Interface Sci.* **2006**, *297* (1), 374-377.
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4
5
6 48. Meth, J. S.; Zane, S. G.; Chi, C.; Londono, J. D.; Wood, B. A.; Cotts, P.; Keating, M.; Guise,
7
8 W.; Weigand, S., Development of Filler Structure in Colloidal Silica-Polymer
9
10 Nanocomposites. *Macromolecules* **2011**, *44* (20), 8301-8313.
11
12 49. Jouault, N.; Zhao, D.; Kumar, S. K., Role of Casting Solvent on Nanoparticle Dispersion in
13
14 Polymer Nanocomposites. *Macromolecules* **2014**, *47* (15), 5246-5255.
15
16 50. Griffin, P. J.; Bocharova, V.; Middleton, L. R.; Composto, R. J.; Clarke, N.; Schweizer, K. S.;
17
18 Winey, K. I., Influence of the Bound Polymer Layer on Nanoparticle Diffusion in Polymer
19
20 Melts. *ACS Macro Letters* **2016**, *5* (10), 1141-1145.
21
22 51. Landau, L. D.; Lifshitz, E. M., *Mechanics: Course of Theoretical Physics*. 3rd ed:
23
24 Butterworth-Heinemann, 1976; Vol. 1.
25
26 52. Holt, A. P.; Griffin, P. J.; Bocharova, V.; Agapov, A. L.; Imel, A. E.; Dadmun, M. D.;
27
28 Sangoro, J. R.; Sokolov, A. P., Dynamics at the Polymer/Nanoparticle Interface in Poly(2-
29
30 Vinylpyridine)/Silica Nanocomposites. *Macromolecules* **2014**, *47* (5), 1837-1843.
31
32 53. Gong, S.; Chen, Q.; Moll, J. F.; Kumar, S. K.; Colby, R. H., Segmental Dynamics of Polymer
33
34 Melts with Spherical Nanoparticles. *ACS Macro Letters* **2014**, *3* (8), 773-777.
35
36 54. Steeman, P. A. M.; Maurer, F. H. J., An Interlayer Model for the Complex Dielectric-Constant
37
38 of Composites. *Colloid Polym. Sci.* **1990**, *268* (4), 315-325.
39
40 55. Carroll, B.; Cheng, S.; Sokolov, A. P., Analyzing the Interfacial Layer Properties in Polymer
41
42 Nanocomposites by Broadband Dielectric Spectroscopy. *Macromolecules* **2017**, *50* (16),
43
44 6149-6163.
45
46 56. Füllbrandt, M.; Purohit, P. J.; Schönhals, A., Combined FTIR and Dielectric Investigation of
47
48 Poly(Vinyl Acetate) Adsorbed on Silica Particles. *Macromolecules* **2013**, *46* (11), 4626-4632.
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4
5
6 57. Havriliak, S.; Negami, S., A Complex Plane Representation of Dielectric and Mechanical
7
8 Relaxation Processes in Some Polymers. *Polymer* **1967**, *8*, 161-210.
9
- 10 58. Rittigstein, P.; Torkelson, J. M., Polymer–Nanoparticle Interfacial Interactions in Polymer
11
12 Nanocomposites: Confinement Effects on Glass Transition Temperature and Suppression of
13
14 Physical Aging. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 2935-2943.
15
16
- 17 59. Cangialosi, D.; Boucher, V. M.; Alegría, A.; Colmenero, J., Physical Aging in Polymers and
18
19 Polymer Nanocomposites: Recent Results and Open Questions. *Soft Matter* **2013**, *9* (36),
20
21 8619-8630.
22
23
- 24 60. Deschamps, T.; Margueritat, J.; Martinet, C.; Mermet, A.; Champagnon, B., Elastic Moduli
25
26 of Permanently Densified Silica Glasses. *Scientific Reports* **2014**, *4*, 7193.
27
28
- 29 61. Guiselin, O., Irreversible Adsorption of a Concentrated Polymer Solution. *EPL (Europhysics*
30
31 *Letters)* **1992**, *17* (3), 225.
32
- 33 62. de Gennes, P. G., Polymers at an Interface; a Simplified View. *Advances in Colloid and*
34
35 *Interface Science* **1987**, *27* (3), 189-209.
36
- 37 63. Zhu, Z.; Thompson, T.; Wang, S.-Q.; von Meerwall, E. D.; Halasa, A., Investigating Linear
38
39 and Nonlinear Viscoelastic Behavior Using Model Silica-Particle-Filled Polybutadiene.
40
41 *Macromolecules* **2005**, *38* (21), 8816-8824.
42
43
- 44 64. Swenson, J.; Smalley, M. V.; Hatharasinghe, H. L. M., Mechanism and Strength of Polymer
45
46 Bridging Flocculation. *Physical Review Letters* **1998**, *81* (26), 5840-5843.
47
48
- 49 65. Carrillo, J.-M. Y.; Cheng, S.; Kumar, R.; Goswami, M.; Sokolov, A. P.; Sumpter, B. G.,
50
51 Untangling the Effects of Chain Rigidity on the Structure and Dynamics of Strongly Adsorbed
52
53 Polymer Melts. *Macromolecules* **2015**, *48* (12), 4207-4219.
54
55
56
57
58
59
60

- 1
2
3
4
5
6 66. Semenov, A. N.; Bonet-Avalos, J.; Johner, A.; Joanny, J. F., Adsorption of Polymer Solutions
7 onto a Flat Surface. *Macromolecules* **1996**, *29* (6), 2179-2196.
8
9
10 67. Auroy, P.; Auvray, L.; Léger, L., Characterization of the Brush Regime for Grafted Polymer
11 Layers at the Solid-Liquid Interface. *Physical Review Letters* **1991**, *66* (6), 719-722.
12
13 68. Schneider, D.; Schmitt, M.; Hui, C. M.; Sainidou, R.; Rembert, P.; Matyjaszewski, K.;
14 Bockstaller, M. R.; Fytas, G., Role of Polymer Graft Architecture on the Acoustic Eigenmode
15 Formation in Densely Polymer-Tethered Colloidal Particles. *ACS Macro Letters* **2014**, *3* (10),
16 1059-1063.
17
18 69. Hore, M. J. A.; Ford, J.; Ohno, K.; Composto, R. J.; Hammouda, B., Direct Measurements of
19 Polymer Brush Conformation Using Small-Angle Neutron Scattering (SANS) from Highly
20 Grafted Iron Oxide Nanoparticles in Homopolymer Melts. *Macromolecules* **2013**, *46* (23),
21 9341-9348.
22
23 70. Holt, A. P.; Bocharova, V.; Cheng, S.; Kisliuk, A. M.; White, B. T.; Saito, T.; Uhrig, D.;
24 Mahalik, J. P.; Kumar, R.; Imel, A. E.; Etampawala, T.; Martin, H.; Sikes, N.; Sumpter, B. G.;
25 Dadmun, M. D.; Sokolov, A. P., Controlling Interfacial Dynamics: Covalent Bonding Versus
26 Physical Adsorption in Polymer Nanocomposites. *ACS Nano* **2016**, *10* (7), 6843-6852.
27
28 71. Wang, S.-Q.; Cheng, S.; Lin, P.; Li, X., A Phenomenological Molecular Model for Yielding
29 and Brittle-Ductile Transition of Polymer Glasses. *The Journal of Chemical Physics* **2014**,
30 *141* (9), 094905.
31
32 72. Zartman, G. D.; Cheng, S.; Li, X.; Lin, F.; Becker, M. L.; Wang, S.-Q., How Melt-Stretching
33 Affects Mechanical Behavior of Polymer Glasses. *Macromolecules* **2012**, *45* (16), 6719-6732.
34
35 73. Oyerokun, F. T.; Schweizer, K. S., Theory of Glassy Dynamics in Conformationally
36 Anisotropic Polymer Systems. *The Journal of Chemical Physics* **2005**, *123* (22), 224901.
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

TABLE OF CONTENTS

