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14. ABSTRACT
The aim of this project is to develop the technology of stabilizing and controlling nanoparticle dispersion in polymers and in particular to apply this technology to the production of high modulus fibers which can be designed to have a variety of multifunctional capabilities. We have found that prestraining a glassy polymer (polystyrene) containing a very small amount (1 wt%) of well dispersed nanoparticles produces a material that has a larger or equivalent modulus, yet, is tougher than the virgin material by a factor of ten as measured by the energy to break. This technology may be used to enhance protective devices for the soldier that are stronger and tougher than present materials without deleterious cost or weight effects. Various

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Generating High Modulus Fibers by Nanoparticle Incorporation with Potential to Introduce Multifunctionality

ABSTRACT

The aim of this project is to develop the technology of stabilizing and controlling nanoparticle dispersion in polymers and in particular to apply this technology to the production of high modulus fibers which can be designed to have a variety of multifunctional capabilities. We have found that prestraining a glassy polymer (polystyrene) containing a very small amount (1 wt%) of well dispersed nanoparticles produces a material that has a larger or equivalent modulus, yet, is tougher than the virgin material by a factor of ten as measured by the energy to break. This technology may be used to enhance protective devices for the soldier that are stronger and tougher than present materials without deleterious cost or weight effects. Various nanoparticle types have been tested although presently it appears that a smaller size is most beneficial (< 5 nm). Small angle neutron scattering has been performed to determine how the nanoparticles and processing affect the polymer conformation which dictates the final materials properties. One of the most unusual findings is that nanoparticles make the material more compressible by introducing free volume, this was not anticipated.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

J. Xu, J. W. Bartels, D. A. Bohnsack, M. E. Mackay and K. L. Wooley, "Hierarchical Inorganic-Organic Nanocomposites Possessing Amphiphilic and Morphological Complexities: Influence of nanofiller dispersion on mechanical performance," Adv Func Materials, 18 (2008) 2733 - 2744.

J. W. Liu, M. E. Mackay and P. M. Duxbury, "Nanoparticle formation by crosslinking a molecule," Europhys Letters, 84 (2008) 46001.

J. Q. Xu, D. A. Bohnsack, M. E. Mackay and K. L. Wooley, "Unusual mechanical performance of amphiphilic crosslinked polymer networks," Journal of the American Chemical Society, 129 (2007) 506-507.

R. S. Krishnan, M. E. Mackay, P. M. Duxbury, A. Pastor, C. J. Hawker, B. Van Horn, S. Asokan and M. S. Wong, "Self-assembled multilayers of nanocomponents," Nano Letters, 7 (2007) 484-489.

R. S. Krishnan, M. E. Mackay, P. M. Duxbury, C. J. Hawker, S. Asokan, M. S. Wong, R. Goyette and P.Thiyagarajan, "Improved polymer thin-film wetting behavior through nanoparticle segregation to interfaces," J. Phys.: Cond Matter, 19 (2007) 356003.

M. A. Holmes, M. E. Mackay and R. K. Giunta, "Nanoparticles for Dewetting Suppression of Thin Polymer Films used in Chemical Sensors," J. Nanopart. Res., 9 (2007) 753-763.

M. E. Mackay, A. Tuteja, P. M. Duxbury, C. J. Hawker, B. Van Horn, Z. B. Guan, G. H. Chen and R. S. Krishnan, "General strategies for nanoparticle dispersion," Science, 311 (2006) 1740-1743.

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(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

J. Xu, D. A. Bohnsack, M. E. Mackay and K. L. Wooley, "Mechanical properties of nanocomposites of functionalized single wall carbon nanotubes with hyperbranched fluoropolymer and poly(ethylene glycol)," Abstracts of Papers of the American Chemical Society, 231 (2006).

D. A. Bohnsack, M. E. Mackay, S. J. Rowan and S. Sivakova, "Telechelic polymers having tunable properties due to bid-inspired nucleobase end groups.," Abstracts of Papers of the American Chemical Society, 228 (2004) U512-U512.

J.W. Liu, M.E. Mackay and P.M. Duxbury, “Simulation of nanoparticle formation by irreversible collapse of unfolded macromolecular precursors”, ACS proceedings in press (2007).

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John Seppala	0.50
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FTE Equivalent:	
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Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

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Total Number:	1

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Introduction. Over the last 50 years the search for high strength, low density materials has lead to macromolecules due to their unique material properties, ability to be easily processed and low cost. One avenue of research to achieve these ultimate properties is gel spinning.[1] In this process the polymer concentration is diluted with specific solvents, thereby reducing intermolecular interactions, to let the macromolecules approach full extension during an orientation processing step prior to solvent removal. By using a very high molecular weight polymer the material's strength is dictated by individual covalent bonds to yield fantastic mechanical properties such as a tensile or Young's modulus (E) of order 300 GPa for polyethylene.[2] This modulus is greater than that of steel, 200 GPa, and considering steel is eight times more dense than most polymers, yields a specific strength an order of magnitude smaller than possible with organic materials. This technology has certainly revolutionized materials science and protected the soldier, however, in the drive to improve the properties of many different polymer types a new strategy was needed.

The discovery of single wall carbon nanotubes (SWNT's)[3] provided a unique reinforcement agent since they have an even larger modulus, of order 1 TPa,[4] due to their unique chemical structure. This, along with their large length on diameter ratio, ~ 500/1, naturally lead to their use in composite materials. Indeed dispersing only 1 vol% SWNT's in a polymer should increase the modulus by approximately 3-times.[5,6] However, homogeneously dispersing even this miniscule amount of nanotubes in polymers has remained elusive. Only through specific processing steps,[7-9] that ensure nanoparticle dispersion, can even a fraction of this enhancement be realized.[10] Yet, in some specific cases, it is possible to functionalize SWNT's to improve their solubility and create a material that approaches this behavior at small concentration.[11]

There are certainly other materials such as graphite platelets[12] which demonstrate mechanical property enhancement in polymeric materials. This is again due to their morphology, inherent strength and large two-dimensional aspect ratio. Yet, the ultimate strength falls short of expectations with the modulus increasing by a factor of two at 5 vol% concentration which is one-third smaller than the anticipated value.[12] In the present work, rather than considering two-dimensional platelets or one-dimensional nanotubes, we proposed to investigate a novel, indirect aspect of nanocomposite reinforcement that does not rely on the inherent nanoparticle mechanical properties.

Results. We drew our inspiration from the unusual behavior spherical nanoparticles display when dispersed in polymers. For example, we have discovered that nanoparticles can reduce the viscosity of polymer melt [9,13] and diffuse over 100-times faster than predicted by the Stokes-Einstein relation[14,15] while imparting multifunctional behavior in the solid material.[16] Since they increase the polymer radius of gyration (R_g) in our system,[17] there must be some effect on the local polymer structure. Note others have also studied this phenomenon through experiment[18] to find an R_g increase or decrease, results that are not necessarily at odds to our findings. In addition to the above unusual effects, a recent theoretical study on nanocomposites[19] has shown the bulk modulus will decrease when nanoparticles are added to a polymeric material (*n.b.* the compressibility is the inverse of the bulk modulus). This is certainly an unusual, and unexpected, prediction; addition of solid objects to a material will make it more compressible. It does suggest that nanoparticles have the potential to affect the local packing or structure of the polymer molecule on the segment level that may affect other material properties.

We tested this by using 78 kD, 6.2 nm diameter cross-linked polystyrene nanoparticles[20] which have every fifth monomer unit crosslinked and a modulus in excess of 1 GPa.[21] They are denoted as PSNP's and were blended with 393 kD linear polystyrene (Scientific Polymer Products) using the rapid precipitation technique to generate a homogeneous mixture.[22] The bulk modulus was determined with a GNOMIX Pressure-Volume-Temperature (PVT) instrument[23] capable of pressures and temperatures of 200 MPa and 200°C, respectively. A sample size of 1 g is required since minute volume changes are measured for a sample surrounded by mercury to ensure a state of homogeneous hydrostatic stress, even below the glass transition temperature (T_g) of the material. The results are shown in Fig. 1A where a decrease in the relative bulk modulus is seen in reasonable agreement to the theoretical prediction of Hooper and Schweizer at low concentration.[19] It is expected that the nanoparticles introduce density fluctuations into the system to produce this effect. Since nanoparticles diffuse approximately 100 times faster than predicted by the Stokes-Einstein-Sutherland relation[14] one may envision such fluctuations induced by their rapid motion.

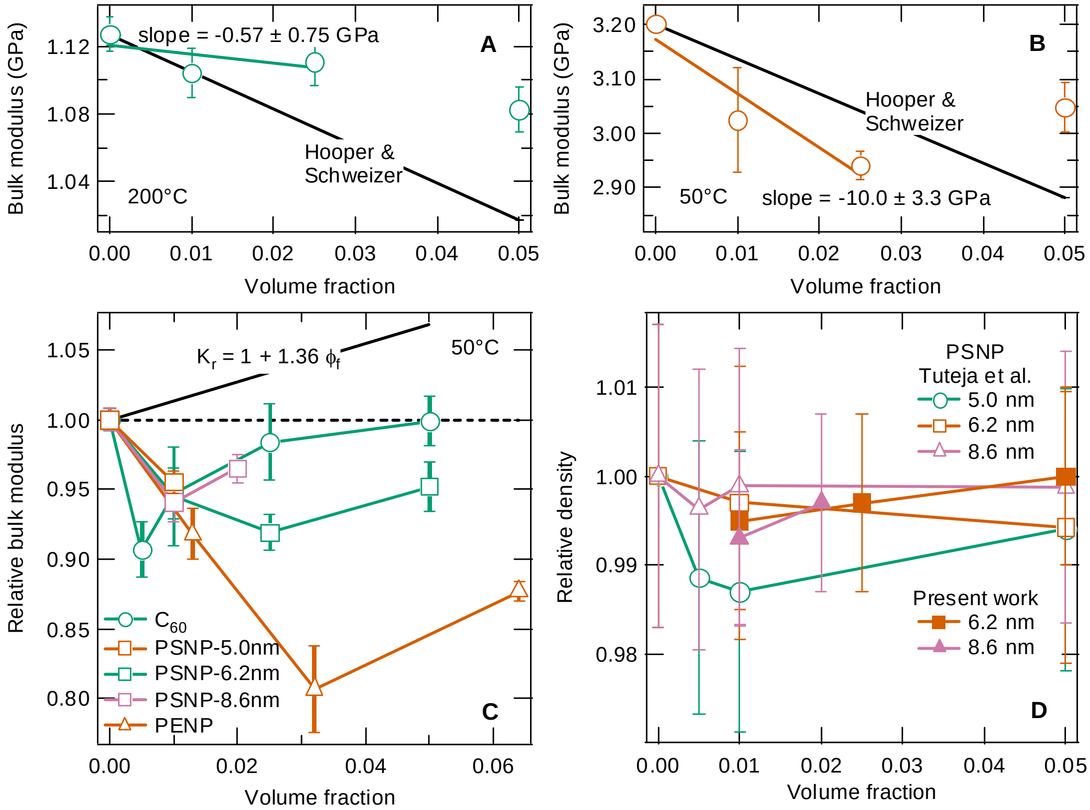

Fig. 1. The bulk modulus of 393 kD polystyrene falls with 78 kD polystyrene nanoparticle addition in both the liquid (200°C, **A**) and glassy (50°C, **B**) states. The prediction by Hooper and Schweizer agrees fairly well with the data at very small volume fraction in the liquid state although it seems to over-predict the effect in general. They find the relative modulus should have a slope of ~ -2 with nanoparticle volume fraction while we find ~ 0.5, a factor of four less. The prediction is given in **B** as a guide to show that the material becomes much more compressible when in the glassy state. (**C**) Relative bulk modulus for 393 kD linear polystyrene blended with C_{60} fullerenes (C_{60}), polystyrene nanoparticles (PSNP) that are 5.0, 6.2 and 8.6 nm in diameter and polyethylene nanoparticles (PENP) at 50°C, below the systems' glass transition temperature. As more nanoparticles are added the relative bulk modulus (K_r) decreases regardless of the nanoparticle type. The fullerenes show a curious concentration dependence most likely due to their small size. Also given is the increase expected for an infinitely stiff particle using the Mori-Tanaka model ($K_r = 1 + 1.36\ \phi_f$). (**D**) The introduction of voidage should produce a slight density reduction which is difficult to confirm with the data that was accurately measured to about 1%. At a volume fraction of 0.01 there should be a ~ 2% reduction in density which is not consistent with the data. Three molecular weight polystyrene nanoparticle systems were used: 41 kD (5.0 nm in diameter), 78 kD (6.2 nm) and 211 kD (8.6 nm), the data appear to be independent of nanoparticle size within experimental error. The density was determined via the Archimedes principle in liquid water at room temperature (~ 22°C).

However, it is apparent that the bulk modulus is affected to a larger degree in the glassy state where the polymer chain is inherently more stiff, see Fig. 1B. We chose to report data at 50°C since little change will occur between this and room temperature, the condition at which we measured the tensile modulus discussed below. Also, the minimum possible temperature to use the instrument was 30°C in its present configuration and it was desired to be in a region of accurate temperature control. Since the nanoparticles can not move under this condition it is clear density fluctuations are created by packing effects. Further, the phenomenon becomes larger at lower temperature, where the chain is stiffer, suggesting the polymer molecule can not wrap round the nanoparticle as effectively as at higher temperature thereby apparently creating a condition of lower relative bulk modulus.

The bulk modulus was determined for a variety of nanoparticles including C_{60} fullerenes,[24] different molecular weight PSNP (41 kD or 5 nm diameter and 211 kD or 8.6 nm diameter) and polyethylene nanoparticles (PENP[22,25]) to ensure the phenomenon was not system specific as shown in Fig. 1C. Here the modulus falls upon nanoparticle addition for all systems. The fullerenes demonstrate complicated behavior and at a mere 0.005 volume fraction produce a bulk modulus reduction in excess of 10%.

However, it is important to realize even at this low concentration there are more than ten times the number of nanoparticles per unit volume than polymer molecules. We believe the fullerenes cause unique behavior since they are very small and have a diameter of 0.76 nm[26] which is smaller than the correlation hole of polystyrene.[27] This may cause the large reduction from packing effects at the monomer length scale which is not the length scale associated with the other larger nanoparticles as discussed below.

Regardless, it is clear that the bulk modulus is reduced for all nanoparticles considered in this study. To ascertain the continuum expectation of how nanoparticles should reinforce the material we find the relative bulk modulus (K_r) and the relative Young's modulus (E_r) using the Mori-Tanaka model[28] considering the presence of voids to model the density fluctuations or packing effects. Here we assume there is a volume fraction of voids (ϕ_V) as well as nanoparticles or filler with volume fraction (ϕ_f) to find

$$E_r \approx G_r = 1+\Delta E_r \phi_f /[1+2S_{1212}\,\Delta E_r] - \phi_V/[1-2S_{1212}], \qquad (1a)$$

$$K_r = 1+\Delta K_r \phi_f /[1+{}^{1}/_{3}S_{kkll}\,\Delta K_r] - \phi_V/[1-{}^{1}/_{3}S_{kkll}] \qquad (1b)$$

for a dilute suspension, G_r is the relative shear modulus. The Eschelby[29] tensor components are given by $S_{1212} = [9K_m-5E_m]/[45K_m+15E_m] = 0.0944$ and $S_{kkll} = [9K_m-E_m]/[3K_m+E_m] = 2.21$ for polystyrene, where K_m and E_m are the matrix bulk and tensile modulus, respectively. The terms ΔK_r and ΔE_r are the specific bulk and tensile modulus for the filler, respectively, obtained by subtracting one from the filler's relative modulus.

If there were no voids then an infinitely stiff particle would produce a bulk modulus increase as shown in Fig. 1C. Now consider the same stiff particle, yet, when voids are present one finds $K_r = 1.014 - 3.80\ \phi_V$ at a filler volume fraction of 0.01. Since the modulus is reduced by 5% at this concentration one finds a void volume fraction of 0.02. This is a significant fraction and should yield a density decrease for the PSNP and linear polymer blend. We have already determined the PSNP to have the same density as linear polystyrene [9] yet, the mixture relative density should be ~ 0.98. The results in Fig. 1D show, within experimental error, that the density remains unchanged suggesting voids are not present although the density is, in one case, within experimental error of the predicted value at a nanoparticle volume fraction of 0.01. Data are from Tuteja *et al.* [30] and our preliminary results.

Before hypothesizing why these seemingly disparate properties emerge, *i.e.* a more compressible material of constant density, the tensile modulus is considered. A TA Instruments RSA 3 dynamic mechanical analyzer was used to determine the tensile modulus using a constant Hencky strain rate of 0.01 s^{-1} for three to five samples under each condition. The error bars in Fig. 2 represent sample to sample variation. While the smallest PSNP shows a substantial modulus increase even at 1 vol% loading, the two larger nanoparticles cause a modulus decrease as shown in Figs. 2A & B. Amazingly, the polyethylene nanoparticle introduces a modulus increase in agreement with the predicted reinforcement created by an infinitely stiff spherical particle calculated *via* eq (1). This is despite the fact that the molecule or nanoparticle is suspected to be quite soft since the bulk material is a liquid at room temperature. A similar modulus increase is found for the fullerenes (Fig. 2A) which is a very stiff nanoparticle.

The results in Fig. 2B for various systems at constant volume fraction are particularly revealing. It is found that CdSe quantum dots[31] with a pyridine steric layer and the similarly sized, yet much softer, 5.0 nm PSNP's samples have an equivalent tensile modulus. This suggests the nanoparticle produces little reinforcement to the composite perhaps due to ineffective stress transfer. Taken with the small, if any, density change leads us to hypothesize regions of low and high polymer density introduced by the nanoparticle as explained below.

We note that polymer molecules near a solid, flat substrate exhibit a region depleted of polymer approximately 1 nm in thickness when the polymer is not strongly attracted to the substrate,[32] as is the case here, to confirm the hypothesis of a low density region. So, a simple model is presented due to packing effects around the nanoparticles in Fig. 2C & D to explain the unusual phenomena we have observed. The exact shape of the low and high density regions or interfaces should not be taken literally where we presume the simplest form of a rectangular prism of length L near the nanoparticle to explain the above data. However, we do not believe the low and high density regions form concentric spherical shells around the nanoparticle. The reason is because we have found the nanoparticles diffuse ~ 100 times faster than predicted by the Stokes-Einstein-Sutherland relation[14] and if surrounded by a high density shell one would expect a slower diffusion process for the nanoparticle.

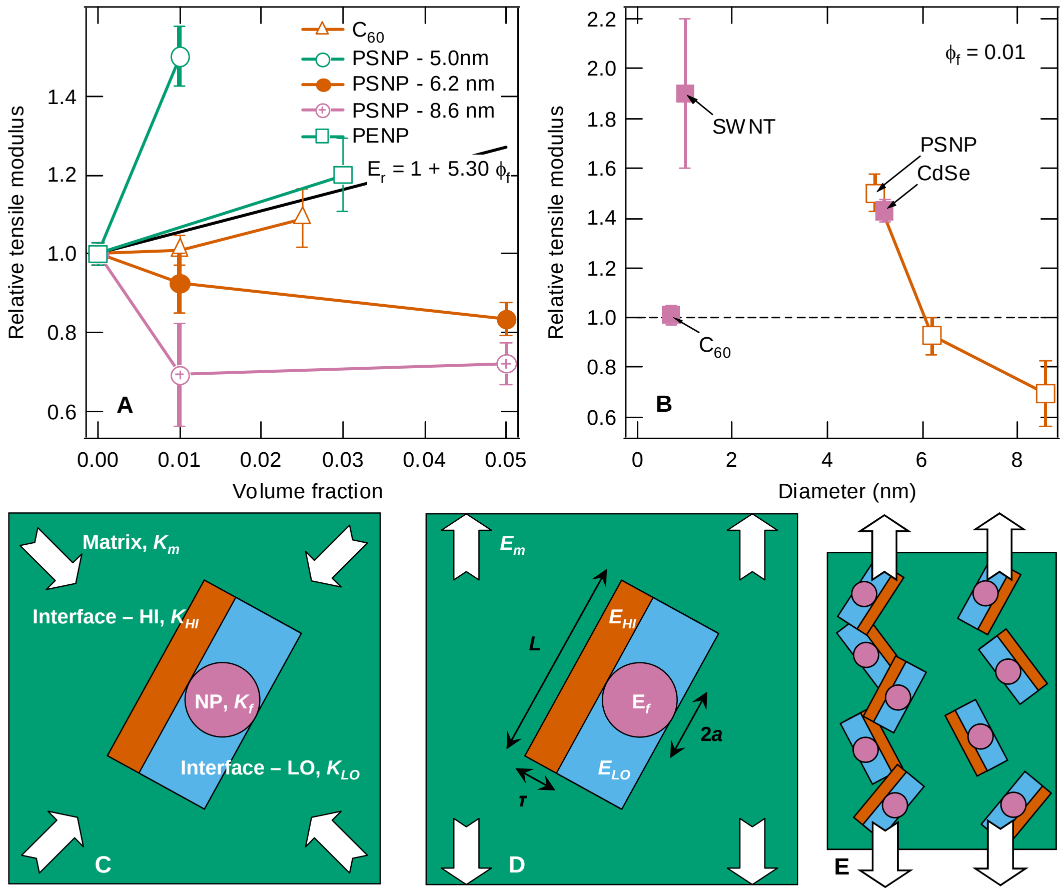

Fig. 2. (**A**) Relative tensile modulus of 393 kD polystyrene as a function of nanoparticle volume fraction. The fullerene nanoparticle (C$_{60}$) produces a small reinforcement effect whereas the polystyrene nanoparticles (PSNP) can yield a large reinforcement or a reduction depending on their diameter (5.0, 6.2 or 8.6 nm). The polyethylene nanoparticle (PENP) also provides a modulus increase and is in agreement with the continuum expectation for an infinitely stiff particle calculated via the Mori-Tanaka relation described in the text ($E_r = 1 + 5.30\ \phi_f$). This is despite the PENP being a liquid at room temperature which should produce a slight modulus reduction. (**B**) Relative tensile modulus for PSNP's as a function of nanoparticle diameter at a constant filler volume fraction of 0.01. The bulk modulus falls in value when nanoparticles are added, however, the tensile modulus increases as the nanoparticle becomes smaller to result in a 50% increase for the smallest PSNP. Quantum dots (CdSe) produce similar reinforcement at the same concentration while smaller fullerenes (C$_{60}$) generate only a minimal increase. Single wall carbon nanotubes (SWNT's) generate a 90% improvement in the tensile modulus despite their very large aspect ratio. The tensile modulus was measured at room temperature (~ 22°C). (**C**) Cartoon showing the compression of the matrix (with bulk modulus of K_m), interfacial component of high density (Interface – HI, K_{HI}), interfacial component of low density (Interface – LO, K_{LO}) and filler or nanoparticle (NP, K_f) which essentially occurs in series. Because series resistances are added in inverse the smallest will dominate, which is K_{LO}, to make the nanocomposite more compressible than the pure matrix. (**D**) In tension there are similar regions for the tensile modulus (E_m, E_{HI}, E_{LO}, E_f, the regions' length scales are also given), however, if the high density region percolates to form a pseudo-fiber it can reinforce the nanocompostie (see left-hand side of **E**). If the high density region does not form a pseudo-fiber one has the weaker low density region acting in series with the other components to make a weaker material in tension (see right-hand side of **E**).

Consider compression first as a way to test this simple hypothesis (Fig. 2C), in this case the individual components; consisting of the matrix, high density interface, low density interface and nanoparticle, will operate in series providing a relative modulus of $1/K_r = \phi_m + \phi_{HI}/K_{HI} + \phi_{LO}/K_{LO} + \phi_f/K_f \approx \phi_m + \phi_{LO}/K_{LO}$ where ϕ_{LO} and K_{LO} are the low density region's volume fraction and relative bulk modulus, respectively. The contribution of the high density region (ϕ_{HI} and K_{HI}) and nanoparticle (ϕ_f and K_f) was neglected since their modulus was assumed to be quite large. Using the above void fraction estimate as ϕ_{LO} ($\approx$ 0.02) at a nanoparticle volume fraction of 0.01, provides K_{LO} of 0.3 relative to pure polystyrene.

This appears a reasonable value since it is not unrealistically small although this should be confirmed in this proposed study through more experimentation and interpretation.

In tension, an individual nanoparticle under this condition (Fig. 2D), must surely exhibit a tensile modulus decrease since the components will also act in series; $1/E_r = \phi_m + \phi_{HI}/E_{HI} + \phi_{LO}/E_{LO} + \phi_f/E_f \approx \phi_m + \phi_{LO}/E_{LO}$, if the low density component's modulus is considered small (the same variables are assigned to the tensile modulus as to the bulk modulus). To increase the modulus we suggest the stronger high density regions percolate to form pseudo-fibers that bridge between nanoparticles. This is explained by considering the average gap between nanoparticles $(2h)$[9] of diameter $2a$ given by $h/a = [\phi_m/\phi_f]^{1/3} – 1$ which is calculated to be 15, 19 and 26 nm for the smallest to largest PSNP's at $\phi_f = 0.01$. Since the smallest PSNP's have an anomalously high tensile modulus the high density interface must propagate of order 7.5 nm on either side of the nanoparticle according to our hypothesis. This is approximately 4 statistical segments[33,34] in length and much smaller than the polymer radius of gyration (17 nm, using the relation of Cotton *et al.*[35]).

We assume the high density region in the smallest PSNP system acts as a pseudo-fiber randomly oriented within the matrix yielding a relative tensile modulus of $E_r = 1 + {}^{1}/_{5}\, \phi_{HI}E_{HI}$ for a fiber with its length much greater than its diameter.[6,36] An estimate of the high density interfacial region's volume fraction is $2a\times2[a+h]\times\tau/8[a+h]^3$ where τ is the thickness and we have assumed the width is the diameter of a nanoparticle, see Fig. 2D. This is clearly a gross approximation, however, we obtain $\phi_{HI} = 0.023$ and calculate $E_{HI} \approx 100$, a rather large modulus. However, gel spinning produces a tensile modulus of order 300 for polyethylene and so it is not unexpected that the pseudo-fibers can produce such reinforcement. Note in this calculation we assumed $\tau = 1.8$ nm which is the statistical segment size for polystyrene[34] and τ could easily be larger in value to affect the volume fraction and hence modulus.

The difference between the case where overlapping and non-overlapping high density regions occurs (Fig. 2E) is expected to be profound. The 8.6 nm diameter PSNP system shows a modulus decrease and assuming the high density regions do not percolate to form a pseudo-fiber the modulus decrease can be calculated as discussed above. We estimate ϕ_{LO} *by* assuming the perturbed region extends 7.5 nm from the edge of the nanoparticle, as found for the 5.0 nm diameter PSNP's, and that the low density interface is $2a$ in thickness and width. Subtracting the volume of a nanoparticle from the volume of a rectangular prism with the above dimensions finds $\phi_{LO} = 0.08$ which is larger than estimated from the bulk modulus (0.02). Of course, the exact dimensions and morphology of the interfacial regions is not truly known and so we are able to merely estimate the tensile modulus of the low density region to be 0.05 - 0.2 for the 8.6 nm diameter PSNP system using the two values for ϕ_{LO}. We can also determine the relative tensile modulus for the intermediate size 6.2 nm diameter PSNP material and find it to be 0.8, lower than the experimental value. Yet, we did not include any potential partial reinforcement introduced by the high density region. So, it is believed the above estimates are able to reproduce the physical principles involved in this novel spherical nanoparticle – linear polystyrene system. However, this will be inverstigated in the proposed project.

To understand how much reinforcement the pseudo-fibers introduce, consider another system such as the rod-like SWNT's. It is important to realize that SWNT's increase the relative modulus of poly(methylmethacrylate) to 1.9 ± 0.3 at 1 vol%,[7] which is not significantly greater than the PSNP system (see Fig. 2B). Indirect reinforcement can be quite powerful in its extent to strengthen materials. Yet, we find the melt viscosity is **decreased** when PSNP's are added to polymer melts[9,13] while SWNT's cause a very large viscosity **increase** which is an undesired processing attribute. So, ease of processibility and a reasonable modulus increase can be obtained when spherical nanoparticles are used.

Polymers show many unusual behaviors and we now consider how packing effects can generate other material properties. For instance, it has been known since the 1950's[37] that drawing polystyrene slightly above its glass transition then quenching to lock in orientation[38] the sample can transform its usual brittle behavior to ductile. It was shown the transition occurs at a certain segmental orientation level that produces subtle packing changes observed through optical birefringence and wide angle X-ray scattering measurements.[39] Since spherical nanoparticles certainly influence segmental, and macromolecular, packing we stretched the samples to various degrees to ascertain their effect on the brittle to ductile transition. Neat 393 kD polystyrene has a brittle to ductile transition at a draw ratio (stretched length to original length) of ~ 2.0 and was found to occur at a smaller value of 1.75 for the two largest PSNP's (Fig. 3). These experiments were carried out by stretching the samples slightly above the

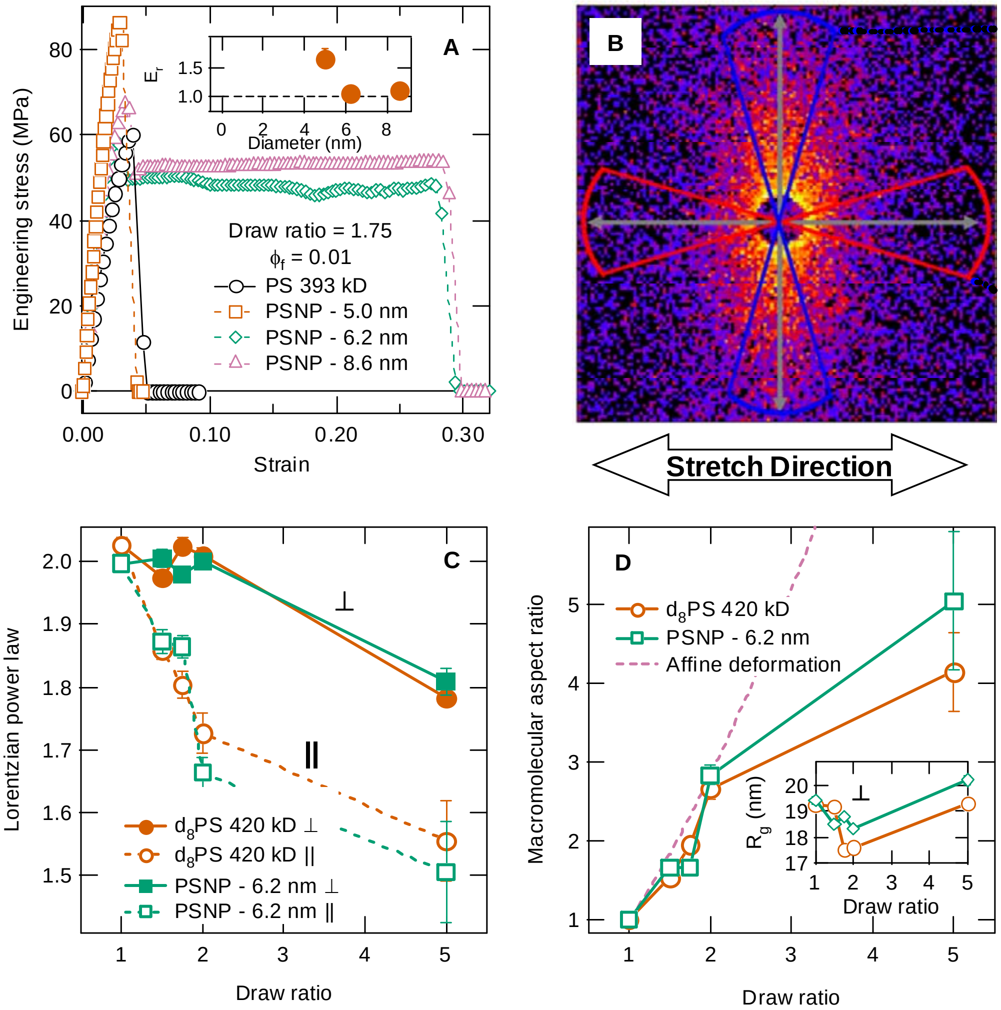

Fig. 3. (**A**) Stretching the samples slightly above their glass transition temperature, 1.75 – times, then quenching the material captures the orientation induced by the stretch. This can make the sample ductile since it fails at ~ 30% strain rather than at 3.5% which only occurs when the larger polystyrene nanoparticles (PSNP) of diameter 6.2 nm and 8.6 nm are blended with 393 kD polystyrene (PS 393 kD). Note there is no loss in the tensile modulus despite the increased ductility. The smallest diameter PSNP (5.0 nm) still exhibited brittle failure, however, the tensile modulus was significantly improved by almost 70%. The inset is the relative tensile modulus as a function of PSNP diameter. (**B**) Anisotropic, neutron scattering, two-dimensional intensity plot for a polystyrene sample that has been stretched at 115°C then rapidly quenched as above. All samples contained 2% 420 kD deuterated polystyrene (d_8PS 420 kD), the requisite amount of polystyrene nanoparticles, 1 vol% or none, and the remainder 393 kD protonated polystyrene. The scattering intensity was obtained parallel and perpendicular to the stretch direction by considering it over a constant angle from the two directions. (**C**) The large wave vector (q) data were fitted to a Lorentzian model (Intensity ~ $[1+q^nL^n]^{-1}$) to extract the Lorentzian power law (n) and length scale (L). If the power law is two then a Gaussian segment distribution is present as occurs at small draw ratios perpendicular (⊥) to the stretch direction. Parallel (||) intensity profiles produce apparent non-Gaussian behavior for all stretch ratios. No true difference is seen between the pure polymer sample and that containing 6.2 nm PSNP's. (**D**) The ratio of the Lorentzian length scale parallel and perpendicular to the stretch direction provides a molecular aspect ratio, which compares well to the radius of gyration ratio (not shown), to demonstrate both the pure and filled sample follow affine deformation until at least a draw ratio of 2. Interestingly, the radius of gyration perpendicular to the stretch direction decreases slightly with draw ratio, as it should, and then rises slightly at larger draw ratios, see text for details of this trend.

glass transition temperature (115°C) at a constant Hencky strain rate of 0.1 s^{-1} to various draw ratios in a TA Instruments RSA 3 then capturing the orientation by quenching the sample. The tensile modulus is increased for the smallest PSNP (inset, Fig. 3A) while the materials becomes more ductile for the two largest nanoparticles. We believe the low density regions present in the liquid polymer allows greater segmental orientation which is resisted in the higher modulus 5.0 nm diameter PSNP system due to the presence of the pseudo-fibers.

We have previously stated the tensile modulus decrease in the 6.2 and 8.6 nm diameter PSNP materials is due to the low density regions and so the above argument fits naturally with this hypothesis. To understand if global macromolecular orientation is also a factor we seeded the samples with 2 wt% 420 kD deuterated linear polystyrene and measured the two-dimensional scattering pattern (Fig. 3B). The intensity signal was collected within a certain angular range (± 20°) parallel and perpendicular to the stretching direction. The averaged intensity (I) versus wave vector (q) data were fitted to a Lorentzian at high wave vector; $I(q) = I(0)/[1+q^nL^n]$, where $I(0)$ is the intensity at zero wave vector. We used this function since the stretched polymer displayed non-Gaussian behavior ($n \neq 2$) at higher draw ratios and L gives some indication of the polymer size. Although the radius of gyration is a better indicator of molecular size, it was difficult to determine because of the limited q-range available at small wave vector. When applicable, L demonstrated the same trends as the radius of gyration. Note that in all cases the same $I(0)$ was used in the data regression since the same amount, 2%, of deuterated polymer was added to each sample that contained 1% 6.2 nm PSNP (or no nanoparticles) with the remainder being 393 kD protonated linear polystyrene.

The tracer polymer showed different behavior parallel to (‖) and perpendicular to (⊥) the stretch direction. While Gaussian behavior is seen perpendicular to the stretch direction up to a draw ratio of 2.0, noticeably non-Gaussian behavior is found for all draw ratios parallel to the processing direction (Fig. 3C). Remarkably though, the same trends are seen with and without nanoparticles. Indeed both essentially follow the affine deformation up to a draw ratio of 2.0 (Fig. 3D), which is where non-Gaussian behavior is seen perpendicular to the draw direction. The inset to Fig. 3D gives the radius of gyration perpendicular to the stretch direction where the molecular size is found to decrease with increasing draw, as it should [38]. However, at high draw ratio it then increases. This is the result of an anomalous fit to the data using the Debye function[40] which is valid only for a Gaussian distribution. We used this function to determine the radius of gyration for this series of experiments since the Guinier region was not accessible. The values are expected to be valid up to a draw ratio of 2.0 (Fig. 3C) and the apparent decrease gives some credence to the conclusions drawn from the Lorentzian model since the curious increase in R_g is in fact an artifact due to the inapplicability of the Debye function.

Since the global polymer dimension is not overtly affected whether nanoparticles are present or not, we conclude nanoparticle induced ductility is a phenomenon related to subtle monomeric packing effects, as discussed earlier,[39] and not to the overall macromolecular conformation. It is clear the nanoparticles affect this phenomenon and local conformation changes induced by the low and high density interfacial regions allows ductile behavior to smoothly progress. Nanoparticles, of order 5 – 10 nm in diameter, are found to influence the brittle to ductile transition and is related to molecular packing effects and potential formation of pseudo-fibers.

In our previous study[22] we considered even larger nanoparticles generated by a chain walking catalyst to make a highly branched polyethylene molecule[41] which was 22 nm in diameter. The heuristic we developed to ensure intimate mixing was to disperse nanoparticles in polymers that have a radius of gyration larger than the nanoparticle radius. This was rationalized *via* a simple Flory theory and is the result of enthalpy gain when the nanoparticle obtains more intimate contact with its surroundings in the blend than in its pure state. Since the radius of gyration for 393 kD polystyrene is ~ 17 nm the polyethylene nanoparticle (PENP) could be readily dispersed to make a well mixed blend. We note the PENP in its pure form is a liquid suggesting the molecules are rather flexible. However, the blend with linear polystyrene shows a modulus increase to the same degree as an infinitely stiff particle (Fig. 2A). When hot drawn at 115°C and quenched, as above, an even larger tensile modulus is obtained. For example, a draw ratio of 1.5 generates a modulus increase in excess of 80% (3.86 GPa compared to 2.12 GPa, Fig. 4).

This unusual behavior is not expected since addition of a liquid to a polymer, for example a plasticizer, generally makes the material more flexible with a lower tensile modulus and usually improves ductility. The PENP also induces ductility at this draw ratio with a strain to fail of 130% compared to 3.5% for neat polystyrene under the same conditions. This corresponds to a 60-fold increase in the tensile energy to break 6×10^7 J/m^3 versus 10^6 J/m^3 obtained by integrating under the engineering stress – strain curve. So, these larger molecules induce increases in both the modulus and ductility under moderate

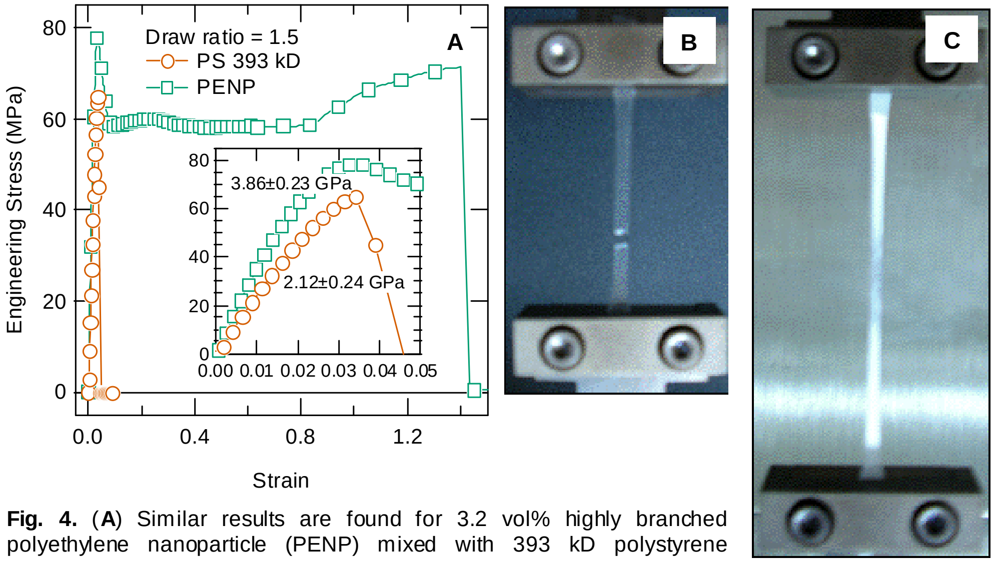

Fig. 4. (**A**) Similar results are found for 3.2 vol% highly branched polyethylene nanoparticle (PENP) mixed with 393 kD polystyrene as seen for other nanoparticle systems described in Fig. 3. In this case the sample was stretched by a factor of 50% at 115°C then rapidly quenched below its glass transition temperature. Note this nanoparticle is much larger in size, 22 nm, and is a liquid in its bulk form at room temperature, yet, it produces a very ductile material that can be stretched over 40-times more than neat polystyrene. However, the tensile modulus is increased by almost a factor of 2 (see inset). An example of the brittle fracture of pure 393 kD polystyrene is shown in (**B**) compared to the ductile behavior for the 3.2 vol% PENP blend (**C**) at a draw ratio of 1.5. In all cases the tensile tests were conducted at room temperature (~ 22°C).

processing conditions which is an unusual combination of properties. The pictures in Fig. 4B & C show the ductile behavior of the blend. Since nanoparticles create other multifunctional properties in polymers,[16] this lead us to call them *solid solvents* to emphasize their peculiarity that is exemplified by the PENP system.

Since the radius of curvature for the PENP is larger than that for the PSNP, ~ 10 nm versus ~ 3 nm, it is believed there is a change in the polymer segment packing near the nanoparticle surface. Rather than a nanoparticle encased within a low density region and a high density region next to it (Fig. 2) we hypothesize a region of high density polymer surrounding the nanoparticle. This is in accord with the tensile modulus increase exhibited by the blend (Fig. 2A) since the reinforcement is equivalent to a particle with infinite modulus. We measured the density of the 2.5 wt% (3.2 vol%) PENP blend and it is 1.03 g/cc within experimental error of the predicted value of 1.04 g/cc again suggesting the formation of high and low density interfacial regions (the density of the pure PENP is 0.81 g/cc[22]). The low density region must be the source of increased ductility although we do not suggest the exact arrangement of the polymer. The formation of pseudo-fibers is not likely to occur since the average gap between the nanoparticles is ~ 40 nm and so we believe the large nanoparticle size relative to the persistence length (1.8 nm) together with the polymer – nanoparticle chemical dissimilarity allows formation of a shell around the nanoparticle of some sort. Low density regions are also present to promote ductility during the drawing operation together with additional reinforcement garnered by the high density regions.

It is not possible to disperse a nanoparticle larger than the polymer radius of gyration without specific chemical modification of the nanoparticle surface,[42] at least according to our experience,[22] thus, the effects outlined above may not occur unless our simple heuristic of relative nanoparticle to polymer size is followed. This may be the reason why increased modulus and ductility has not been simultaneously observed for a nanocomposite since the modulus can be increased, however, the strain to break suffers.[43] We note also that the yield stress is increased (*i.e.* Fig. 3A) creating a stiffer, stronger and more ductile nanocomposite which we believe is the result of the nanoparticle geometry, a sphere, of high surface area to volume ratio combined with chemical dissimilarity between the two components to induce useful packing effects in the polymer that ultimately makes the nanocomposite stronger.

Summary. We have found very unusual and usually contradictory mechanical properties. As described above, we have found that nanoparticles can make the materials more compressible while increasing the tensile modulus. In addition, we have also shown the tensile modulus can increase while the material subsequently becomes more ductile. These are nanoscale phenomena which are manifested at the sub-molecular level and due to delicate changes in the polymer packing. We hope in the future to continue this study and ascertain the exact nature of the local packing.

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