Goal:
Polymer nanocomposites (PNCs) have been of considerable interest to the materials community for the last several decades. Various property improvements are obtained when nanoparticles (NPs) are added to polymers. However, the molecular and structural basis behind the enhancement is still unclear. There is growing evidence to suggest that mechanical reinforcement results when NPs with a bound polymer layer (BPL) form a percolating structure, where the BPL interacts with free chains between neighboring NPs, subsequently creating network with NPs as nodes and polymer chains as bridges (Fig. 1). We propose to advance our understanding of the structure-dynamics-property relationships using X-ray photon correlation spectroscopy (XPCS) and rheology on model PNCs: silica (SiO$_2$) NPs dispersed in a poly(2-vinyl pyridine) (P2VP) matrix where a dispersion structure of NP, a BPL structure, and macroscopic mechanical properties have been well characterized. By tuning the interparticle distance between neighboring NPs with different NP loadings, we aim to develop a better understanding of the formation of the proposed percolation network and the contribution towards mechanical enhancement.

Research Design
To prepare the model PNC, we are collaborating with Dr. Alexei Sokolov (U. Tennessee) who established sample preparation for spherical SiO$_2$ NPs dispersed in a P2VP matrix even at high NP loadings [1]. SiO$_2$ NPs were synthesized according to the Stober method and stabilized in ethanol. The average radius ($R$) of SiO$_2$ NPs was 8.8 nm with a polydispersity of 1.1. P2VP (molecular weight of $M_n = 38$ kg/mol with a polydispersity of 1.1) was purchased from Polymer Source. The advantage of this PNC system is to precisely control the interparticle distance ($L$) between neighboring NPs by changing NP loadings (Figure 1). The NP volume fractions were 1, 6, 16, and 27% and the corresponding $L$ values were determined to be 66, 12, 4.8, and 1.4 nm, respectively, based on small-angle X-ray scattering experiments.

XPCS experiments were conducted at the Beamline 11-ID of National Synchrotron Light Source-II (Brookhaven National Laboratory). The nanocomposite films were placed in a thermal vacuum stage and heated from 150 °C to 190 °C at 10 °C intervals. Intensity autocorrelation functions ($g_2$) were generated by integrating the speckle pattern across the time interval.

Rheological characterization was performed on a TA HR2 Discovery rheometer using an 8 mm parallel plate geometry. Melt-pressed samples were loaded at 150 °C with a gap height of 0.7 mm and heated to 190 °C. Small amplitude oscillatory frequency sweeps were performed across a frequency range of $\omega = 0.1 – 100$ rad/s at a strain of $\gamma = 0.1\%$. Strain amplitude was found to be within linear viscoelastic regime according to strain ramps from $\gamma = 0.001 – 100\%$ at $T = 150$ °C and $\omega = 10$ rad/s. Frequency sweeps were performed from 150 – 190 °C at 10 °C intervals. Time-temperature superposition principle was applied when appropriate.

**Fig. 1.** Proposed NP distributions in a polymer melt: (a) When NP loading is beyond a critical value, the NPs (indicated in gold circles) with BPL (indicated in blue) are in direct contact, resulting in a glassy bridge responsible for a solid-like property of PNCs; (b) When NP loading is below the critical threshold, the NPs cluster through the BPL, forming a flexible “rubbery” bridge; (c) When NP loading is dilute enough, NPs do not interact each other, i.e., no structural bridge formation. The chains indicated in black correspond to free polymer chains.
Results
Fig. 2 shows representative normalized $g_2$ functions for the SiO$_2$/P2VP PNCs at 180 °C. $g_2$ is normalized as $[(g_2\text{-baseline})/\text{contrast}] + 1$ so that the contrast and baseline are the same for each correlation function. The characteristic relaxation time increases with NP concentration. We found that $g_2$ is described by a simple exponential or compressed exponential function (shown by solid lines in Fig. 2). At NP contents greater than 6%, a second slower relaxation process was identified, now accurately modeled using a double compressed exponential function. Further data analysis clarified that the characteristic relaxation times for the 1% loading PNC correspond to the self-diffusive motion of the individual NP, suggesting no structural bridges. The macroscopic mechanical properties identified by rheology concluded that the 1% loading PNC is a viscoelastic liquid. For the 6% loading PNC, the fast relaxation times were very close to those for the 1% loading PNC, while the relaxation times for the slow mode are several times slower. The rheology experiments identified an approach to gelation at 6%, while the NP loadings of 16% and 27% are identified as a gel point and a solidification point, respectively, which are consistent with a previous report [2]. We hence anticipate that the slow dynamics emerged in the high loading PNCs are attributed to the collective dynamics of the structural (rubbery or glassy) bridges responsible for the enhanced mechanical properties. Hence, the XPCS results reveal the microscopic dynamics of the percolate “strand” formed in a polymer matrix.

IMPACT ON PI’S CAREER
Funds from the ACS PRF allowed the PI to launch a new research direction in the polymer field. The PRF-driven preliminary results are used to seek continuation funding from other agencies.

IMPACT ON STUDENTS
Funds from the ACS PRF have supported one graduate student (Mr. Daniel Salatto). We anticipate that the student will publish the above experimental results by Spring 2020. He also participated in other research programs and contributed two recent papers as a co-author [3,4]. He also delivered one oral talk at the 2019 APS March meeting and one poster at the 2019 CFN DOE Triennial Review (June, 2019). Through the project, he gained various advanced characterization techniques at the US national laboratory facilities.

References