Supporting Information for Structural Characterization of CVD Custom-Synthesized Carbon Nanotube/Polymer Nanocomposites in Large Amplitude Oscillatory Shear (LAOS) Mode: Effect of Dispersion Characteristics in Confined Geometries

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Low-torque limit and instrument/sample-inertia limits for oscillatory strain amplitude sweep and oscillatory frequency sweep. As can be seen in Figure S1 (a), the storage modulus for neat PVDF is orders of magnitude above the low-torque limit and instrument/sample-inertia limits, proving that the observed high-frequency $\omega^2$ scaling behavior is due to the inherent viscoelastic behavior of the materials studied in this work. We also checked the low-torque limit in a typical strain sweep experiment for neat PVDF and the results confirm that the viscoelastic response of our samples is well above this limit (orders of magnitude higher, Figure S1 (b)).

![Figure S1](image_url)

**Figure S1.** (a) Low-torque and instrument/sample-inertia limits shown for oscillatory frequency sweep of PVDF. (b) Low-torque limit shown for the oscillatory strain amplitude sweep of PVDF. The procedure used for calculation of the low-torque and the instrument/sample-inertia limits can be found in ref\textsuperscript{1}. 

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\textsuperscript{1} Low-torque limit and instrument/sample-inertia limits for oscillatory strain amplitude sweep and oscillatory frequency sweep.
**Damping factor and complex viscosity.** Figures S2 (d), (e), and (f) show complex viscosity of neat PVDF and CPNs at different angular frequencies and different strain amplitudes. Pötschke et al.\(^2\) investigated the frequency dependency of complex viscosity of polycarbonate(PC)/CNT at different nanotubes concentrations. They observed only a small frequency dependence for neat PC. However, the complex viscosity of PC/CNT showed a strong frequency dependence and it decreased as the frequency increased. We observed the same behavior. As can be seen in Figure S2, neat PVDF shows a small frequency dependence with a tendency toward a Newtonian plateau at low frequencies. However, the diverging complex viscosity observed for CPNs in the low-frequency region signifies the existence of CNT structures in these samples.
**Figure S2.** Damping factor ($\tan \delta$) and complex viscosity ($|\eta^*|$) of neat PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes synthesized at different temperatures for strain amplitude of (a) & (d) 1%, (b) & (e) 10%, and (c) & (f) 100% using the cone-plate geometry (at a truncation of 47μm and cone tip angle of 1°) at 240°C.

**Effect of gap-size on frequency sweep response.** To verify the confinement effect of the large agglomerates between the rheometer plates, the storage modulus was investigated as a function of the gap-size using the cone-plate and parallel plate geometries. For this purpose, the storage modulus was measured using a frequency sweep test for CPNs at several gap-sizes of 47μm, 200μm, and 400μm (see Figure S3). The presence of wall-slip at the metal plate and polymer melt interface is known to greatly affect the apparent rheological response of molten polymers. Therefore, it is necessary to check whether there are any possible errors arising from slippage at the polymer-plates interfaces. According to Figure S3 (a), the storage modulus has the same value in different gap-sizes for neat PVDF. Thus, it can be concluded that the slippage at metal plates-
polymer melt interface is virtually nonexistent in the examined gap-sizes and the corresponding shear rates associated with the experimental conditions.

To investigate the effect of the gap-size on the rheological behavior of CPNs, CNT$_{950}$ with poor dispersion state and CNT$_{650}$ with a homogeneous dispersion state in the PVDF matrix were chosen to study. For the well-dispersed structure of CNT$_{650}$, the storage modulus is almost independent of the gap-size (Figure S3(b)). Moreover, as expected, the $G'$ curves exhibit a plateau at lower frequencies for this sample, indicative of a solid-like response. The solid-like viscoelastic response at low frequencies results from the formation of a percolated three-dimensional network of CNT$_{650}$. The most notable effect of increasing gap-size was observed for the nanocomposites containing CNT$_{950}$. CNT$_{950}$/PVDF nanocomposite effectively undergoes a solid-to-liquid transition with increasing the gap-size (see Figure S3(c)). In contrast to the gap-size of 47μm, at the gap-sizes of 200μm and 400μm, the values of $G'$ for CNT$_{950}$/PVDF nanocomposite was almost near to the $G'$ of the neat PVDF, and no enhancement in the storage modulus was observed. Thus, the data in Figure S3 confirm that the dramatic increase of $G'$ for poorly-dispersed systems at the small gap-size of 47μm is due to the formation of jammed structures upon confinement between the two measuring plates.
Figure S3. Gap-size dependency of storage modulus ($G'$) of (a) neat PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes synthesized at (b) 650°C and (c) 950°C using cone-plate geometry (at a truncation of 47μm and cone tip angle of 1°) and parallel-plate geometry at gap-sizes of 200μm and 400μm at 240°C.

Dimensionless storage modulus versus strain amplitude for different CNTs concentrations.

Figure S4. Dimensionless storage modulus versus strain amplitude for well-dispersed CNT$_{650}$/PVDF and poorly-dispersed CNT$_{950}$/PVDF nanocomposites containing different CNTs loading. Highlighted points illustrate critical strain amplitude (transition from linear viscoelastic to nonlinear viscoelastic behavior).

**Frequency dependence of LAOS behavior of CPNs.** It is worthwhile to mention that the transition to nonlinearity in both poorly- and well-dispersed nanocomposites is frequency-invariant, as shown in Figure S5.
Figure S5. Frequency dependency of dimensionless storage modulus of CNT/PVDF nanocomposites containing 1.0 wt% of carbon nanotubes synthesized at 650°C and 950°C using cone-plate (at a truncation of 47 μm and cone tip angle of 1°) at 240°C.

Nanofiller concentration dependence of LAOS behavior of CPNs. A similar two-step yielding process was observed at extremely low CNT₉₅₀ contents (e.g., 0.3 wt%, Figure S6). Moreover, increasing the content of the nanofillers, not only leads to an increase in the intermediate elastic modulus plateau but also delays the transition to a highly nonlinear response towards larger strain amplitudes. This also verifies that breakage of weak inter-aggregates links in the poorly-dispersed system under confinement of rheometer plates plays the major role in the first step of yielding.

Figure S6. LAOS behavior of well- and poorly-dispersed systems, namely CNT₆₅₀/PVDF and CNT₉₅₀/PVDF at different concentration of CNT.

Output shear stress response. Figure S7 shows the intra-cycle input strain and intra-cycle output stress signals for two values of the applied strain amplitudes (1% and 620%) for neat PVDF. Figure S7 (a) is consistent with a typical linear response, demonstrating a single-harmonic sinusoidal output stress signal. As the strain amplitude exceeds the linear viscoelastic limit, the distortions in
stress signal response become apparent. In Figure S7 (b), the output stress signal is entirely non-
sinusoidal for strain amplitude of 620%.

**Figure S7.** Intra-cycle output shear stress $\tau_{\text{raw}}$ response and intra-cycle input strain waveform $\gamma_{\text{raw}}$ and the corresponding Lissajous-Bowditch loops on different projections during measurements of the viscoelastic properties of the pure PVDF melt at strain amplitude of (a) 1% (linear regime (ii)) and (b) 620% (nonlinear regime (iv)) and frequency of 10rad/s.
Dimensionless 3D Lissajous-Bowditch loops.

**Figure S8.** 3-dimensional Lissajous-Bowditch loops for PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes synthesized at different temperatures using a cone-plate geometry (at a truncation of 47μm and a cone tip angle of 1°) at 240°C and an angular frequency of $\omega = 10$rad/s.
**Gap-size dependency of Lissajous-Bowditch loops.** To check the gap-size dependency of the intra-cycle viscoelastic behavior of neat PVDF and CPNs, we picked Lissajous loops at strain amplitude of 4% (first point of the first yielding process) and 250% (last point of the intermediate plateau). The Lissajous loops superimpose on each other at a strain amplitude of 250% for all samples and no gap-dependency is observable. The same behavior was observed for PVDF and the well-dispersed CNT\textsubscript{650} nanocomposite at a strain amplitude of 4%. However, as expected based on the data in Figures S3 and 8, the Lissajous loops do not collapse on each other at a strain of 4% for the poorly-dispersed CNT\textsubscript{950} system. As can be seen, Lissajous loops at smaller gap sizes enclose a smaller gap-sizes corresponding to a larger elasticity for the poorly-dispersed CNT\textsubscript{950} system. This confirms that the observed gap-dependence trend in the poorly-dispersed systems is mainly due to the confinement effect at smaller gap-sizes.

![Figure S9](image-url)  
**Figure S9.** Gap-size dependency of Lissajous-Bowditch loops (on elastic projection) of neat PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes synthesized at 650°C and 950°C using a 25mm cone-plate geometry (at a truncation of 47μm and cone tip angle of 1°) and a 25mm parallel-plate geometry at gap-sizes of 100μm and 400μm at 240°C and a strain frequency of \( \omega = 10\text{rad/s} \).
Lissajous-Bowditch loops of PVDF at an angular frequency of 1 rad/s. It is worth mentioning that even if we decrease the frequency to 1.0 rad/s, we can still see the self-intersection at large deformations in viscous projection.

![Figure S10](image-url)

**Figure S10.** Lissajous-Bowditch loops of neat PVDF at strain amplitudes of 620% and 1000% using a cone-plate geometry with a truncation of 47 μm and a cone tip angle of 1° at 240°C and a strain frequency of ω = 1 rad/s.

Elastic (S) and viscous (T) intra-cycle nonlinearity indices.

![Figure S11](image-url)

**Figure S11.** Elastic (S) and viscous (T) intra-cycle nonlinearity indices as a function of imposed strain amplitude for PVDF and CNT/PVDF nanocomposites containing 2.7 wt% of carbon nanotubes synthesized at different temperatures.

**Dissipated energy per unit volume.** Yziquel et al.⁴ have shown that the area of the Lissajous curve in one cycle can be used to determine the dissipated energy per unit volume at each corresponding strain. The dissipated energy is defined by the following expression:
\[ E_d = \oint_{\text{cycle}} \tau \, d\gamma \quad \text{Eq.1} \]

Figure S12 shows the Lissajous loops of total stress versus strain in one cycle for the strain of 10% in regime (ii) for pure PVDF, CNT\textsubscript{650}/PVDF, and CNT\textsubscript{950}/PVDF. Based on Eq.1 the area of the graphs in Figure S12 shows the dissipated energy per cycle. In this regime, CNT\textsubscript{650}/PVDF is in the linear viscoelastic framework, while CNT\textsubscript{950}/PVDF undergoes a significant nonlinearity. Thus, the area of the nanocomposite sample containing CNT\textsubscript{650} is almost close to neat PVDF. However, as expected, due to the microstructure evolution in regime (ii) for CNT\textsubscript{950}/PVDF, this CPN has the largest area of the Lissajous loops, confirming the higher dissipative character for this sample in the regime (ii).

![Lissajous loops](image)

**Figure S12.** Elastic Lissajous-Bowditch curves at strain of 10% for PVDF, CNT\textsubscript{650}/PVDF and CNT\textsubscript{950}/PVDF nanocomposites containing 1.0wt% of carbon nanotubes.
Nonlinear dynamic moduli of PVDF and CPNs.

Figure S13. Nonlinear viscoelastic measures of $\eta_L$ and $\eta_M$ as a function of strain amplitude at a strain frequency of 10 rad/s for neat PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes synthesized at 650°C and 950°C using cone-plate geometry for gap-size of 47μm at 240°C.
**Effect of frequency on viscous** ($T$) **intra-cycle nonlinearity index.** As can be seen in Figure S14, a decrease in frequency leads to a reduction in intra-cycle shear-thickening behavior. The nonlinear measures showed an intra-cycle shear-thickening behavior at medium strain amplitudes and a gentle intra-cycle shear-thinning behavior at larger strain amplitudes for the frequency of $5\text{rad/s}$. Further decrease in frequency ($\omega=1\text{rad/s}$) resulted in a strong intra-cycle shear-thinning behavior in all regions of the nonlinear framework. At lower frequencies, i.e., longer experiment time in one cycle, polymer chains have enough time for rotation and configurational rearrangement within the period of an oscillating cycle. However, by increasing the frequency at large strain amplitudes, the response of the polymer chains will be limited to stretching of the chemical bonds and there is no time for polymer chain orientation in the experiment time scale.$^{5-6}$ Consequently, at high frequencies (shorter time scale) chain stretching becomes important and control the nonlinear viscoelastic behavior, which leads to strong intra-cycle shear-thickening behavior, while at low frequencies intra-cycle shear-thinning was observed.
**Figure S14.** Viscous (T) intra-cycle nonlinearity index as a function of imposed strain amplitude for neat PVDF at (a) \( \omega = 1 \text{rad/s} \), (b) \( \omega = 5 \text{rad/s} \) and (c) \( \omega = 10 \text{rad/s} \).

**Gap-size dependency of the nonlinear parameters of the poorly-dispersed CNT\textsubscript{950}/PVDF nanocomposite.**

![Graphs showing S and T as a function of strain amplitude for different gap-sizes at 550°C and 950°C.](image)

**Figure S15.** Elastic (S) and viscous (T) intra-cycle nonlinearity indices as a function of strain amplitude for poorly-dispersed CNT\textsubscript{550}/PVDF, CNT\textsubscript{850}/PVDF, and CNT\textsubscript{950}/PVDF nanocomposites containing 1.0wt% of carbon nanotubes at different gap-sizes using a 25mm parallel plate geometry at strain frequency of \( \omega = 10 \text{rad/s} \).

**Maximum moduli in amplitude sweep test for PVDF and PVDF/CNTs.**

**Table S1.** Maximum storage modulus (\( G' \)) and loss modulus (\( G'' \)) in amplitude sweep test for PVDF and PVDF/CNTs

|                | PVDF | CNT\textsubscript{550} | CNT\textsubscript{650} | CNT\textsubscript{750} | CNT\textsubscript{850} | CNT\textsubscript{950} |
|----------------|------|------------------------|------------------------|------------------------|------------------------|------------------------|
| \( G'_\text{max} \) [kPa] | 7    | 26                     | 9.8                    | 7.9                    | 157                    | 408                    |
| \( G''_\text{max} \) [kPa]  | 16.8 | 18.9                   | 19                     | 17.9                   | 21.7                   | 49.8                   |
REFERENCES

(1) Ewoldt, R. H.; Johnston, M. T.; Caretta, L. M., Experimental challenges of shear rheology: how to avoid bad data. In *Complex fluids in biological systems*, Springer: 2015; pp 207-241.

(2) Pötschke, P.; Fornes, T.; Paul, D. Rheological behavior of multiwalled carbon nanotube/polycarbonate composites. *Polymer* 2002, 43 (11), 3247-3255.

(3) Hatzikiriakos, S. G. Wall slip of molten polymers. *Progress in Polymer Science* 2012, 37 (4), 624-643.

(4) Yziquel, F.; Carreau, P.; Tanguy, P. Non-linear viscoelastic behavior of fumed silica suspensions. *Rheologica Acta* 1999, 38 (1), 14-25.

(5) Ferry, J. D., *Viscoelastic properties of polymers*. John Wiley & Sons: 1980.

(6) Song, H. Y.; Park, S. J.; Hyun, K. Characterization of Dilution Effect of Semidilute Polymer Solution on Intrinsic Nonlinearity $Q_0$ via FT Rheology. *Macromolecules* 2017, 50 (16), 6238-6254.