Large Amplitude Oscillatory Shear Flow: Microstructural Assessment of Polymer Nanocomposites, Hydrogels, and Interfaces

Kamkar, Milad
Large Amplitude Oscillatory Shear Flow: Microstructural Assessment of Polymer Nanocomposites, Hydrogels, and Interfaces

by

Milad Kamkar

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

GRADUATE PROGRAM IN CHEMICAL AND PETROLEUM ENGINEERING

CALGARY, ALBERTA

MARCH, 2020

© Milad Kamkar 2020
Abstract

Final properties of polymeric materials e.g., polymer nanocomposites, hydrogels, etc., significantly depend on the microstructure, e.g., dispersion quality of the nanofillers, of the final product. Hence, in-depth exploration and characterization of the microstructure of these materials is of great importance from both an industrial and an academic point of view. In this regard, rheometry has been widely used as a powerful tool to investigate the micro- and nano-structural features of complex fluids. Regarding structural characterization, rheometry provides more reliable information compared to imaging techniques. Many research studies have been performed on the structure-property relationships for various polymeric systems using linear viscoelastic data obtained under small-amplitude oscillatory shear (SAOS) flow. Although SAOS tests provide useful information about the relationship between the rheological properties and microstructure, it should be noted that SAOS flow is limited to a narrow strain or stress region, i.e., ultra-small deformation and linear viscoelastic behavior. Therefore, rheological measurements under intermediate- and large-strain amplitudes have the potential to reveal important additional information regarding aspects of materials response not accessible via linear rheology.

Because of the mentioned reasons, large-amplitude oscillatory shear (LAOS) flow has attracted much attention from both academia and industry. Hence, this Ph.D. thesis has focused on LAOS behavior of a wide range of complex polymeric materials, including polymer nanocomposites, hybrid polymer nanocomposites, hydrogels, and interfaces. This study has a dual achievement: (i) better understanding of the network structure of the polymer/nanomaterial-based fluids using LAOS techniques, and (ii) in-depth knowledge of nonlinear viscoelastic behavior of complex fluids.
That is, upon improvement the network structure of viscoelastic materials, e.g., improving the dispersion quality of the nanofillers in a polymeric matrix, we observed that: (1) the onset of inter- and intra-cycle viscoelastic nonlinearity shifts to lower deformations, (2) the extent of intra-cycle elastic nonlinearity decreases in LAOS region while the intra-cycle viscous nonlinearity increases, and (3) the nonlinearity of interfaces changes from strain-softening to weak strain overshoot. In addition to characterization of the network structure of the mentioned systems by LAOS, for the first time we showed the effects of confinement and wall-slip on LAOS data of polymeric materials.

Keywords: Nonlinear Rheology, Large-Amplitude Oscillatory Shear (LAOS) Flow, Microstructure Characterization, Polymer Nanocomposites, Hydrogels, Complex Fluids
Acknowledgements

I greatly appreciate my supervisor, Dr. Uttandaraman Sundararaj, whose resourceful expertise and knowledge made my PhD career a productive experience. He was always a source of a great deal of support and encouragement. I would like to extend my appreciation to my supervisory committee members and external examiners, Dr. E P L Roberts, Dr. Milana Trifkovic, Dr. Jeffrey Giacomin, and Dr. Rahil Koshnazar because of their insights and comments. I would also like to express my gratitude to Dr. Gerald G. Fuller at Stanford University and polymer processing group (PPG) members at University of Calgary, particularly, Dr. Mohammad Arjmand and Dr. Soheil Sadeghi.

The financial support from the Natural Science and Engineering Research Council (NSERC) of Canada is highly appreciated.

The deepest gratitude goes to my family because of their unconditional support and encouragement.
To:

To God for being my greatest strength and blessing me with the power to fulfil this journey. For being my best and most faithful friend and for always accompanying me. Thank you my God for guiding me along the way, for every obstacle that made me stronger. This achievement belongs to you God.

To my mother Freshteh, my father Majid, and my sisters Mona and Mahsa for their heartfelt supports. I am grateful to them and feeling honored to dedicate my entire work to the precious persons of my life.
# Table of Contents

1 Chapter 1-Introduction........................................................................................................1
1.1 CNT-based polymer nanocomposites (Ch. 3)..............................................................3
1.2 Hybrid CNT-based polymer nanocomposites (Ch. 4)................................................5
1.3 Effect of mixing method on microstructure of CNT-based polymer nanocomposites (Ch. 5) ......................................................................................................................6
1.4 Bio-hydrogels (Ch. 6) ....................................................................................................7
1.5 Viscoelastic response of graphene oxide assemblies at interfaces (Ch. 7) ..............9
1.6 Background .............................................................................................................10
  1.6.1 Parallel plates geometry ...................................................................................10
  1.6.2 Cone and plate geometry .................................................................................11
  1.6.3 Small amplitude oscillatory shear (SAOS) rheometry. ....................................12
  1.6.4 Large amplitude oscillatory shear (LAOS) rheometry. ...................................13
1.7 References ..............................................................................................................15

2 Chapter 2 - Materials, Processing and Characterization ...........................................25
2.1 Methodology and Chapters’ Overview ..................................................................25
2.2 Materials ................................................................................................................26
  2.2.1 Poly(vinylidene Fluoride) (PVDF) ...............................................................26
  2.2.2 Polystyrene (PS)............................................................................................26
  2.2.3 Alumina .........................................................................................................27
  2.2.4 Gaseous reagents .........................................................................................27
  2.2.5 Iron (III) Nitrate Nonahydrate (Fe(NO3)3.9H2O) .........................................27
  2.2.6 Multi-walled carbon nanotubes (MWCNTs) ..............................................27
  2.2.7 Methacrylic anhydride ..................................................................................28
  2.2.8 Irgacure 2959 ...............................................................................................28
  2.2.9 Oil phase. ......................................................................................................28
  2.2.10 Graphene oxide (GO) synthesize. ..............................................................28
2.3 Sample preparation ..................................................................................................29
  2.3.1 Phase (i) .......................................................................................................29
  2.3.2 Phase (ii) .....................................................................................................29
  2.3.3 Phase (iii) .....................................................................................................29
  2.3.4 Phase (iv) .....................................................................................................30
2.4 Characterizations......................................................................................................30
  2.4.1 Compression molding ...................................................................................30
  2.4.2 Transmission electron microscope (TEM) imaging. .....................................31
  2.4.3 Light microscope (LM) imaging ..................................................................31
  2.4.4 Scanning electron microscopy (SEM) imaging ............................................31
  2.4.5 Broadband electrical conductivity. ..............................................................31
  2.4.6 Electromagnetic interference (EMI) Shielding. ..........................................31
  2.4.7 Bulk and interfacial rheology .......................................................................32
  2.4.8 Interfacial tension .........................................................................................33
Chapter 3 - Structural Characterization of CVD Custom-Synthesized Carbon Nanotube/Polymer Nanocomposites in Large Amplitude Oscillatory Shear (LAOS) Mode: Effect of Dispersion Characteristics in Confined Geometries

3.1 Abstract
3.2 Introduction
3.3 Experimental
3.3.1 Materials synthesis and characterization.
3.3.2 CNT characterization.
3.3.3 Nanocomposite characterization
3.3.4 Broadband electrical conductivity.
3.3.5 Rheology.
3.4 Results and discussion
3.4.1 Structural and morphological characterization of nanofillers and nanocomposites.
3.4.2 Broadband electrical conductivity.
3.4.3 Oscillatory frequency sweep.
3.4.4 Strain amplitude sweep (inter-cycle viscoelastic behavior).
3.4.5 Gap-size dependence of multi-step yielding.
3.4.6 Lissajous-Bowditch plots (intra-cycle viscoelastic behavior).
3.4.7 Intra-cycle nonlinear viscoelastic parameters.
3.5 Conclusions
3.6 References

Chapter 4 - Application of Nonlinear Rheology to Assess the Effect of Secondary Nanofiller on Network Structure of Hybrid Polymer Nanocomposites

4.1 Abstract
4.2 Introduction
4.3 Experiments and material characterizations
4.3.1 Nanocomposites preparation
4.3.2 Transmission electron microscopy
4.3.3 Light transmission microscopy
4.3.4 Rheology
4.4 Results and discussion
4.4.1 Nanofiller characterization
4.4.2 Transient shear stress response and image analysis
4.4.3 Storage modulus recovery
4.4.4 Effect of secondary nanofiller on LAOS flow and nonlinear viscoelastic parameters
4.4.5 Lissajous-Bowditch plots
4.5 Conclusions
4.6 References

Chapter 5 - The Key Role of Processing in Tuning Nonlinear Viscoelastic Properties and Microwave Absorption in CNT-based Polymer Nanocomposites

5.1 Abstract
5.2 Introduction
5.3 Experimental Section
List of Tables

Table 4-1: Agglomerate area for nanocomposites ................................................................. 91

Table 5-1: Characterizing elastic nonlinearity in response to imposed LAOS deformation 38 ... 128

Table 5-2 Characterizing viscous nonlinearity in response to imposed LAOS deformation 38 ... 128
List of Figures and Illustrations

Figure 1-1: Schematic illustration of the strain sweep test at a fixed frequency. This sweep test can be used for determining the linear and nonlinear viscoelastic regions. In the linear region (small amplitude oscillatory shear(SAOS)), the storage ($G'$) and loss ($G''$) moduli are independent of the applied deformation at a fixed frequency and the resulting output stress waveform is a sinusoidal. However, in the nonlinear region (large amplitude oscillatory shear (LAOS)), the storage and loss moduli become a function of the strain amplitude ($G'(\gamma_0)$ and $G''(\gamma_0)$) at a fixed frequency and the resulting stress waveform is no longer a simple sinusoidal wave........................................................................................................ 1

Figure 1-2: (a) parallel plates and (b) cone and plate geometries of rotational rheometers....... 11

Figure 3-1: (a) TGA, (b) DTG, (c) onset point and carbon purity, (d) length and diameter, and (e) powder conductivity of CNTs synthesized at various temperatures. (f) Agglomerate area ratio and relative transparency of thin cuts of 2.0wt% CNT/PVDF nanocomposites. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society .............................................. 44

Figure 3-2: SEM micrographs and schematics illustrating the structure of carbonaceous materials formed at various synthesis temperatures. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society ................................................................................................................. 45

Figure 3-3: LM images of microtomed CNT/PVDF nanocomposites with 2.0wt% CNT loading. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society. ......................................................... 46

Figure 3-4: Schematics depicting dispersion state and physical feature of CNTs synthesized at various temperatures within the PVDF matrix. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society. ................................................................................................................. 47

Figure 3-5: Broadband electrical conductivity of nanocomposites containing CNTs synthesized at various temperatures. The critical frequency for CNT$_{550}$ and CNT$_{750}$ nanocomposites containing 2.7wt% of the nanofiller is shown by red arrows. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society. ......................................................... 50

Figure 3-6: Storage modulus ($G'$) and loss modulus ($G''$) of neat PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes synthesized at different temperatures for strain amplitudes of (a) and (d) 1%, (b) and (e) 10%, and (c) and (f) 100% using cone-plate geometry (at a truncation of 47μm and cone tip angle of 1°) at 240°C. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society. ......................................................... 52

Figure 3-7: Oscillatory amplitude sweep response of neat PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes synthesized at different
temperatures for strain amplitudes of $\gamma_0=0.1-1000\%$ at an angular frequency of $\omega = 10\text{rad/s}$ using cone-plate geometry (at a truncation of 47$\mu$m and cone tip angle of 1°) at 240°C. For sake of easier comparison, storage modulus $G'$ (open black symbols) and loss modulus $G''$ (solid red symbols) values were normalized with respect to their maximum values (Table S1 of Supporting Information, Appendix A). Data points indicated by arrows were used in Figure 3-9 to obtain the Lissajous-Bowditch loops. The insets show magnified $G'$ response of CNT$_{750}$/PVDF and magnified $G''$ response of CNT$_{850}$/PVDF and CNT$_{550}$/PVDF for strain amplitudes of 0.1-10%. As shown by vertical dotted lines, four distinct regimes in the viscoelastic response of poorly-dispersed samples are identifiable as the strain amplitude increases. The first regime (i) corresponds to the linear viscoelastic region (LVR). In the second regime (ii) $G'$ decreased into an intermediate plateau (third regime (iii)), and in the last regime (iv) there is a dramatic decrease in $G'$. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society.

Figure 3-8: Gap-size dependence of storage modulus of neat PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes synthesized at different temperatures using cone-plate geometry (at a truncation of 47$\mu$m and cone tip angle of 1°) and parallel-plate geometry at gap-sizes of 100$\mu$m, 400$\mu$m, and 1000$\mu$m at 240°C. Figure S16 of Appendix A shows the loss modulus at different gap-sizes. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society.

Figure 3-9: Dimensionless Lissajous-Bowditch loops for PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes synthesized at different temperatures using cone-plate geometry (with a truncation of 47$\mu$m and a cone tip angle of 1°) at 240°C. Projections on the elastic ($\tau - \gamma$) and viscous ($\tau - d\gamma/dt$) planes are presented at strain amplitudes of $\gamma_0= 1, 4, 39,$ and 620% and an angular frequency of $\omega =10\text{rad/s}$. In the upper most left plot, the star symbol shows the strain for flow reversal and the circle symbol shows the maximum stress point. Triangle symbol shows the location of starting the second half-cycle of oscillation. Figure S8 of Appendix A shows the 3-dimensional Lissajous Loops. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society.

Figure 3-10: Elastic ($S$) and viscous ($T$) intra-cycle nonlinearity indices as a function of imposed strain amplitude for PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes synthesized at different temperatures. See Figure S11 of Appendix A for similar results for nanocomposites containing 2.7wt%. Figure S15 of Appendix A shows the gap-size dependency of elastic ($S$) and viscous ($T$) intra-cycle nonlinearity indices for the poorly-dispersed CNT$_{950}$/PVDF nanocomposite. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society.

Figure 4-1: (a) and (b) TEM images of MnO$_2$NW at low and high magnifications, respectively, (c) XRD patterns of synthesized MnO$_2$NW. Reprinted (Figure 1c) with permission from A. Shayesteh Zeraati, S. A. Mirkhani and U. Sundararaj, Enhanced Dielectric
Figure 5-3: Oscillatory amplitude sweep response of PS/MWCNT nanocomposites containing (a) and (b) 0.5vol.% and (c) and (d) 2.0vol.% of carbon nanotubes for strain amplitudes of $\gamma_0=0.1-1000\%$ at an angular frequency of $\omega = 1$ rad/s using a parallel-plate geometry at a gap-size of 0.2 mm at 230 °C. Open symbols represent loss modulus ($G''$) and solid symbols represent storage modulus ($G'$). The star symbols show the critical strain amplitude (linear to nonlinear transition).

Figure 5-4: (a), (b), and (c) local viscosities: minimum strain rate viscosity $\eta_M'$ and large strain rate viscosity $\eta_L'$; (d), (e), and (f) local elastic measures: minimum strain modulus $G_M'$ and large strain modulus $G_L'$; (g), (h), and (i) intra-cycle viscoelastic parameters: strain-stiffening ratio ($S$) and shear-thickening ratio ($T$). Data have been obtained at angular frequency of $\omega = 1$ rad/s using a parallel-plate geometry at 230 °C for PS/2.0 vol.% MWCNT. See Figures S2 and S3 for the same results at MWCNT concentrations of 0.5 and 1.0 vol.% respectively.

Figure 6-1: Side view for specimen between rheometer’s plates (parallel-plate geometry).

Figure 6-2: Scanning electron microscopic (SEM) micrographs illustrating the structure of GelMA hydrogels at different GelMA concentrations.

Figure 6-3: Oscillatory amplitude sweep response of gelatin-based hydrogels for strain amplitudes of $\gamma_0=0.1-100\%$ at an angular frequency of $\omega = 1$rad/s using parallel-plate geometry at room temperature, (a) 10% (w/v) GelMA hydrogel, (b) 15% (w/v) GelMA hydrogel, and (c) 20% (w/v) GelMA hydrogel. Data points indicated by arrows were used in Figure 6-4 to obtain the Lissajous-Bowditch loops. The insets show magnified $G'$ response for strain amplitudes of 10.0-100.0%. Black dotted circles indicate yield strain. Red dotted circles indicate the onset of inter-cycle strain-stiffening behavior.

Figure 6-4: 3-D Lissajous-Bowditch curves for different concentrations of the polymer in GelMA hydrogel at strain amplitudes of $\gamma_0 = 10, 26, 50, \text{ and } 70\%$ are shown in first row. (a) elastic and (b) viscous Lissajous-Bowditch curves for 10% (w/v) GelMA hydrogel; (c) elastic and (d) viscous Lissajous-Bowditch curves for 15% (w/v) GelMA hydrogel; (e) elastic and (f) viscous Lissajous-Bowditch curves for 20% (w/v) GelMA hydrogel. (g) and (h) elastic and (i) and (j) viscous Lissajous-Bowditch curves for 10% (w/v) GelMA hydrogel (black line), 15% (w/v) GelMA hydrogel (gray line), and 20% (w/v) GelMA hydrogel (light blue line) at strain amplitude of 10% (linear regime) and strain amplitude of 70% (nonlinear regime).

Figure 6-5: Intra-cycle nonlinear measures; (a), (b), and (c) are local dynamic viscosities: minimum strain rate viscosity $\eta_M'$ and large strain rate viscosity $\eta_L'$; (d), (e), and (f) are local elastic measures: minimum strain modulus $G_M'$ and large strain modulus $G_L'$; (g), (h), and (i) intra-cycle viscoelastic parameters: strain-stiffening ratio ($S$) and shear-thickening ratio ($T$). Data were obtained at angular frequency of $\omega = 1$rad/s using parallel-plate geometry at room temperature.

Figure 7-1: (a) Raman spectra, (b) ATR-FTIR spectra, (c) TGA, and (d) and (e) TEM images of GO (scale bar = 200nm).
Figure 7-2: (a) and (b) evolution of interfacial elastic ($G_s'$) and loss ($G_s''$) moduli of aqueous dispersion of GO at air and oil interfaces at 0.1 and 0.3vol% of GO. Time sweep test has been conducted instantly after loading the samples at strain amplitude of $\gamma_0 = 0.1\%$ and angular frequency of $\omega = 0.5\text{rad/s}$. (c) interfacial tension of aqueous suspension of GO at air and oil interfaces at 0.1 and 0.3vol% of GO. The rheological tests have been conducted at ambient temperature using a du Noüy interfacial geometry. We used standard deviation for error bars. ................................................................. 173

Figure 7-3: interfacial elastic ($G_s'$) and loss ($G_s''$) moduli of aqueous suspension of GO at (a) and (b) oil and (c) and (d) air interfaces at 0.1 and 0.3vol% of GO as a function of strain amplitude at an angular frequency of $\omega = 1.0\text{rad/s}$. The rheological tests have been conducted at ambient temperature using a du Noüy interfacial geometry. ................................. 177

Figure 8-1: Effect of reinforcing network structure of nanofillers in polymeric systems on intra-cycle viscoelastic parameters (strain-stiffening ratio ($S$) and shear-thickening ratio ($T$)). The elastic intra-cycle nonlinearity occurs mainly due to chain deformation and stretching at large strain amplitudes. Hence, improvement in network structure leads to decrease in intra-cycle elastic nonlinearity. In contrast to intra-cycle elastic nonlinearity, intra-cycle viscous nonlinearity becomes more pronounced upon strengthening the polymeric system network structures, which can be correlated to the orientation of the rigid components of the systems in the flow direction................................................................. 183

Figure 8-2: Effect of reinforcing the interface of liquid-liquid (oil/water-GO) and air-liquid (air/water-GO) on inter-cycle interfacial viscoelastic response. This figure shows that by improving the interface upon changing the top phase (i.e., replacing air with oil), the type of inter-cycle nonlinearity changes from strain-softening to weak strain overshoot behavior. The same behavior was observed in chapter 7 by enhancing the interfacial network with increasing the content of nanomaterials at air/water interface. ................. 184

Figure 8-3: Effect of confinement of the agglomerates of nanofillers between the plats of the rheometer on inter- and intra-cycle nonlinear behavior of polymeric nanocomposites. The confinement effect impacts both inter- and intra-cycle response. That is, the poorly-dispersed systems containing gap spanning aggregates follow a two-step inter-cycle yielding process upon exceeding the limit of the linearity. Moreover, these systems feature an intra-cycle dissipative response in medium amplitude region (positive $T$ index). Additionally, the distortion in output shear stress response and Lissajous- Bowditch plots is higher for systems containing confined structures. ......................................................... 186

Figure 8-4: Effect of wall-slip phenomenon on inter- and intra-cycle nonlinear response of the polymeric hydrogels. Wall-slip phenomenon impacts both inter- and intra-cycle behavior. The inter-cycle behavior upon transition into nonlinear regime is type III (weak strain overshoot) in the presence of wall-slip. While, we observed type II inter-cycle behavior after eliminating wall-slip error. Moreover, wall-slip also affects the onset and extent of both elastic and viscous intra-cycle nonlinearity. ................................................................. 188
List of Symbols, Abbreviations and Nomenclature

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>APAM</td>
<td>Alberta Polymer Asymmetric Minimixer</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>CPN</td>
<td>CNT-based Polymer Nanocomposite</td>
</tr>
<tr>
<td>DTG</td>
<td>Derivative of Thermogravimetric</td>
</tr>
<tr>
<td>LAOS</td>
<td>large-amplitude Oscillatory Shear</td>
</tr>
<tr>
<td>LM</td>
<td>Light Microscopy</td>
</tr>
<tr>
<td>LVR</td>
<td>Linear Viscoelastic Region</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multiwall Carbon Nanotube</td>
</tr>
<tr>
<td>NW</td>
<td>Nanowire</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PVDF</td>
<td>Poly(vinylidene Fluoride)</td>
</tr>
<tr>
<td>SE</td>
<td>Shielding Effectiveness</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SAOS</td>
<td>Small-amplitude Oscillatory Shear</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
“You must never be fearful of what you are doing when it is right.”

Marie Curie
Chapter 1-Introduction.

Dynamic oscillatory shear tests are conducted on the materials by applying a sinusoidal deformation and measuring the resulting mechanical response. These tests can be divided into two regimes, namely linear viscoelastic regime, conducted under small amplitude oscillatory shear (SAOS), and nonlinear viscoelastic regime, conducted under large amplitude oscillatory shear (LAOS). Figure 1-1 shows the viscoelastic response (e.g., storage modulus $G'$) to an input oscillatory deformation in both linear and nonlinear regimes.

![Figure 1-1: Schematic illustration of the strain sweep test at a fixed frequency.](image)

Input strain

$\gamma(t) = \gamma_0 \sin \omega t$

Log $G' [\text{Pa}]$

Log strain amplitude $[\gamma_0] [-]$

Linear regime (SAOS)

Nonlinear regime (LAOS)

It should be mentioned that in the linear viscoelastic framework the deformation is sufficiently small (i.e., $\gamma_0 \approx 10^{-2} - 10^{-1}$ for homopolymer melts and polymer solutions) that rheological parameters (e.g., storage modulus $G' (\omega)$ and loss modulus $G'' (\omega)$) are independent of strain
amplitude. Hence, the measured output oscillatory stress waveform is also sinusoidal (see Figure 1-1). However, beyond linear viscoelastic regime, $G'(\omega, \gamma_0)$ and $G''(\omega, \gamma_0)$ become strain dependent, leading to distortion in periodic output stress waveform due to the excitation of the higher harmonics. The nonlinear dynamic tests at large deformations are referred to as LAOS tests.

Although linear viscoelastic tests under SAOS flow offer useful information about the relationship between the microstructure and rheological properties, SAOS tests are limited to narrow strain or stress regions. Hence, these tests would be unable to distinguish complex fluids with similar nano-structures or molecular structures. Additionally, in most industrial processing techniques, materials experience large and rapid deformations; i.e., in the nonlinear region.

Because of the mentioned limitations of SAOS approach and to simulate industrial processing situations (i.e., large and rapid deformations), the LAOS technique has drawn great attention. Moreover, since the strain amplitude and frequency can be controlled independently, LAOS tests can cover a wide range of nonlinear conditions with respect to time and deformation. Hence, LAOS approach provides a powerful framework enabling us to map out a rich phenomenology of inter- and intra-cycle nonlinearities, playing an important role in the structure–property relationship of the filler-polymer systems and thus engineering design.

The first studies investigating the nonlinear response of viscoelastic materials under LAOS flow were published from 1960s to 1970s.\textsuperscript{1-8} However, technical problems (e.g., hardware and software limitations) hindered the development of LAOS approach in those decades. In 1993 Giacomin and Dealy\textsuperscript{9} provided information about LAOS protocols and sources of information on the analysis of LAOS experiments. However, it should be borne in mind that with respect to rheological response of complex materials (e.g., polymer nanocomposites and hydrogels), the nonlinear viscoelastic properties still remain largely unexplored. So, the theoretical underpinnings of the nonlinear
response of viscoelastic materials under LAOS flow are still poorly understood. In recent years, new rheometers with high torque resolution and strong computational power enabled us to study the nonlinear rheological response of viscoelastic materials with great accuracy. Hence, in this Ph.D. thesis, we aim to improve the current state of LAOS. To achieve this, we investigate nonlinear viscoelastic response of a wide range of complex viscoelastic systems (e.g., polymer nanocomposites, hybrid polymer nanocomposites, hydrogels, and interfaces) under LAOS deformations.

1.1 CNT-based polymer nanocomposites (Ch. 3)

Carbon nanotube (CNT) has emerged as one of the most popular nanofillers in the polymer composite industry since it can significantly enhance final properties (e.g., electrical, mechanical, rheological, and so forth) at low filler contents. It has been widely demonstrated that a key factor to control the electrical, mechanical, electromagnetic interference (EMI) shielding effectiveness (SE), and rheological properties of CNT-based polymer nanocomposites (CPNs) is the network structure of CNTs. Hence, monitoring CPNs’ network structure formation is of utmost significance. The CNT network structure can be controlled by manipulating physical (e.g., aspect ratio) or chemical features (e.g., functionalization and doping) of individual nanotubes. For instance, increased aspect ratio leads to reduced percolation threshold in polymer nanocomposites; and the doping of CNTs with other chemical elements (e.g., nitrogen) is a simple way to manipulate CNTs’ properties, which in turn, dramatically affect final properties of polymer nanocomposites, e.g., dielectric properties and electrical conductivity. As an example, nitrogen doped CNTs (N-CNTs)/polymer nanocomposites have the potential to be used for charge storage applications, such as embedded capacitors.
As mentioned earlier, the other important factor that controls the final properties CNT-based polymer nanocomposites, is physical features (e.g., length and diameter) of individual CNTs. In our previous works,\textsuperscript{19-22} we were able to synthesize CNTs with different physical properties employing the chemical vapor deposition (CVD) method. In our works, physical structure of CNTs was fine-tuned by changing the temperature, synthesis time or catalyst. Significant differences in electrical conductivity, dielectric properties, EMI shielding effectiveness, and thermal properties of the CPNs were observed upon changing the physical structure of the CNTs.\textsuperscript{19-22} For instance, Keteklahijani et al.\textsuperscript{21} studied the effect of synthesis temperature of CNTs on final properties of CNTs and their nanocomposites. The authors showed that synthesis temperature has a significant effect on the structural features of CNTs and, consequently, on CNT network formation within the polymeric matrix.

Hence, deeper investigation of microstructure for a wide range of systems including nanotubes featuring different physical or chemical structures is of great importance for both academia and industry. The interrelationship between polymer nanocomposite microstructures and their rheological properties makes rheometry a versatile approach to study the nanofiller network architecture. For instance, Cipiriano et al.\textsuperscript{16} and Wu et al.\textsuperscript{23} have studied the effect of CNT network structure on linear viscoelastic properties under SAOS flow by changing the aspect ratio of CNTs in a polymeric matrix. However, nonlinear viscoelastic characterization of CNT-based polymer nanocomposites remains largely unknown. Hence, since the current literature is missing a fundamental study of nonlinear rheological behavior of nanocomposites containing CNTs with various physical structures, we employed medium and large amplitude oscillatory shear (MAOS and LAOS) flows to characterize these flocculated systems for the first time. We utilized this protocol, because MAOS and LAOS can provide greater insight into characterization of complex
fluids as they cover a wider domain of deformation or time scale. As a result, MAOS and LAOS
tests are more applicable to real flow fields that exist in most polymer processing techniques.

Chapter 3 of this thesis provides the following results: (i) employing MAOS and LAOS
techniques to obtain a better understanding of the effect of the morphology of CNTs on network
formation of nanotubes within a polymer matrix and (ii) enhancing exploration of intra-cycle
viscoelastic parameters of CPNs in MAOS and LAOS regions using well-defined synthesized
CNTs and nanocomposites thereof.

1.2 Hybrid CNT-based polymer nanocomposites (Ch. 4)

Another promising method to change the network structure of CNTs’ in a polymeric medium is
by addition of a secondary filler. For instance, Liu et al. have shown that adding clay as a
secondary filler into an epoxy matrix improved the dispersion and distribution of CNTs without
harming electrical conductivity or mechanical performance. The authors claimed that CNTs have
an affinity for clay leading them to become more exfoliated and better networked in these
composites. In another work, Shayesteh et al. showed that addition of MnO2 nanowires
(MnO2NWs) as secondary nanofillers can dramatically enhance dielectric properties of CNT-
based polymer nanocomposites. The authors postulated that the enhanced dielectric properties of
the hybrid nanocomposites is due to the better dispersion state of CNTs upon addition of
MnO2NW. In the mentioned works, the authors just focused on the final electrical properties of
the hybrid polymer nanocomposites and the literature is missing a fundamental understanding of
the network structure of the hybrid polymer nanocomposites from a rheological point of view.

In regard to polymer nanocomposites, the microstructure of nanofillers across a polymer medium
has been widely studied employing direct microscopic observations and indirect estimation
methods. The former includes optical microscopy (OM), scanning electron microscopy (SEM),
atomic force microscopy (AFM), transmission electron microscopy (TEM), etc. However, microscopic observations can only provide information about a small part of the sample in the selected cross section, thus, they are not cumulative representative of the dispersion state of CNTs 
27-28.

However, melt rheological response is a strong indicator of the dispersion state and microstructure of nanofillers in the bulk.29-33 Many research studies have been carried out to establish structure-property relationships for various nanocomposite systems using the linear viscoelastic data obtained under SAOS flow.14,30,34-36 However, the SAOS-based analysis methods are not adequate to fully understand the microstructure of polymer nanocomposites,37 necessitating an in-depth investigation of the nonlinear behavior of hybrid polymer nanocomposites. Therefore, a fundamental question remains to be addressed: how does addition of secondary nanofillers affect the viscoelastic response of polymer nanocomposites beyond the linear limit?

Hence, to evaluate the microstructure of the hybrid polymer nanocomposites, the nonlinear rheological properties of CNT/MnO2NW polymer nanocomposites under LAOS and steady shear flow were studied in chapter 4 of this thesis. Using stress decomposition method38 coupled with the proposed method by Ewoldt et al.39 (i.e., Chebyshev coefficients), the nonlinearity of the generated hybrid polymer nanocomposites was used to evaluate the quality of CNTs dispersion. Microscopic imaging at micro- and nano-scale (optical and electron microscopy) was also employed to validate the rheological data.

1.3 Effect of mixing method on microstructure of CNT-based polymer nanocomposites
(Ch. 5)

CNTs are usually synthesized in the form of entangled aggregates and bundles. This aggregation behavior is an obstacle to achieve desired dispersion of the nanotubes. To obtain a desirable
dispersion state of CNTs, it is essential to break down the CNT aggregates to an acceptable level. Hence, achieving a proper dispersion quality of these nanofillers in polymer matrices is one of the major challenges in polymer processing industry. Solution mixing and melt mixing techniques are among the most common processing methods to overcome this challenge and disperse CNTs in a medium.\textsuperscript{40-43}

During the last decades, the effect of processing conditions on the dispersion quality of CNTs in polymer composites prepared by melt mixing has been intensively investigated.\textsuperscript{40-41, 44} Likewise, many authors focused on the influence of solution mixing conditions on the dispersion state of the CNTs.\textsuperscript{45-46} In another study, Ke et al.\textsuperscript{47} compared the effect of solution mixing and melt mixing on linear viscoelastic properties of the CNT-based polymer nanocomposites. The authors reported higher linear storage modulus for solution-mixed samples compared to melt-mixed samples. This observation was correlated to stronger global constraint effect caused by CNTs on the long relaxation of polymer chains in solution-mixed samples.

However, to the best of our knowledge, there is no work in the literature systematically studying the effect of processing techniques on nonlinear rheological properties of polymer nanocomposites using LAOS flow. Accordingly, in chapter 5, we provided an in-depth understanding of the effect of processing techniques on CNT network structure using nonlinear viscoelastic results obtained under LAOS flow. Moreover, the effect of CNT dispersion and network formation on EMI shielding performance of nanocomposites was assessed in X-band frequency. The results were also verified by imaging techniques.

1.4 Bio-hydrogels (Ch. 6)

Hydrogels are cross-linked network of hydrophilic polymers with the capability to retain a large volume fraction of water.\textsuperscript{48} Numerous hydrogels have been developed based on natural and/or
synthetic polymers with tunable mechanical and biological properties. These hydrogels have potential applications in regenerative medicine such as 3D hepatic tissues, vascular tissue reconstructions, tissue adhesives, drug delivery, and wound healing. Among the bio-hydrogels, gelatin methacryloyl (GelMA) hydrogel (also known as gelatinmethacrylate, methacrylated gelatin, meth-acrylamide modified gelatin, or gelatin methacrylamide) has been widely used because of its physical and biochemical properties for many different applications ranging from tissue engineering to drug and gene delivery.

GelMA is a covalently cross-linked hydrogel reacted via photoinitiated radical polymerization method. GelMA hydrogels is a tunable biomaterial for tissue engineering and wide applications of these hydrogels require them to cover a wide range of mechanical behavior. Their mechanical properties not only regulate biological behavior of the embedded cells, but also determine the final properties of the developed tissues. With respect to the mechanical behavior of hydrogels, the vast majority of publications have examined linear viscoelastic properties under ultra-small deformations. However, in practical applications, the designed hydrogels would undergo large and rapid deformations, necessitating investigation of the nonlinear viscoelastic behavior of hydrogels.

Hence, in chapter 6, we investigated the nonlinear viscoelastic behavior of chemically cross-linked gelatin-based hydrogels (GelMA), featuring different concentrations of the hydrogel precursor, under LAOS deformations. It was shown that the nonlinear viscoelastic response of the GelMA hydrogel can be tuned by changing concentration of the hydrogel precursor. Our results also show that the viscoelastic data of hydrogels are highly afflicted by artefacts, even at small deformations, such as those due to wall-slip. Hence, to investigate the viscoelastic response under large strains, for the first time we provide a novel method to eliminate error arising from wall-slip.
in rheological measurements of chemically cross-linked hydrogels containing a large fraction of water. Thus, methods developed in chapter 6 can be used to guide the development and improvement of new hydrogels that can mimic the unique viscoelastic properties of native extracellular matrix.

1.5 Viscoelastic response of graphene oxide assemblies at interfaces (Ch. 7)

Oil/water emulsions stabilized by colloidal particles, have been investigated since the early 20th century.58-59 These systems are commonly called Pickering emulsions. Silica nanoparticles60-61 and graphene oxide (GO) nanosheets62 have been widely used for the purpose of oil-in-water or water-in-oil stabilization. For instance, Binks et al.60 have shown that hydrophobized silica particles can stabilize water/oil emulsions.

It has been well-established that the emulsification mechanism exhibited by nano-sized materials is based on particle adsorption at the oil/water interface.63 To achieve a nanoparticle-stabilized emulsion, the following conditions must be fulfilled: (1) the particles must be surface-active and/or get pinned to the interface; (2) the particles have to be stable at the interface (i.e., they have to remain trapped at the interface even when the interface is strongly compressed or deformed); and (3) the particles have to form an interfacial assembly that has high mechanical strength. The dual nature of GO nanosheets (hydrophilicity and hydrophobicity) combined with their flexible structure make them a versatile candidate for nanoparticle-stabilized emulsification of oil in water. Hydrophilic functional moieties (e.g., hydroxyl, carboxylic, and epoxy groups) on the surface of GO nanosheets make the hydrophobic basal plane of nanosheets strongly surface-active. Due to this dual nature, GO nanosheets can be anchored at the oil and water interfaces, leading to stable emulsions.
Imperiali et al.\textsuperscript{64} tuned the surface activity of GO nanosheets by varying the carbon to oxygen ratio. The authors claimed that the GO nanosheets can be deposited at either a water–air or a water–oil interface by controlling the carbon to oxygen ratio. They also studied the mechanical properties of GO film at water/air interfaces employing compression/expansion experiments in a Langmuir trough and shear rheometry (creep and recovery). However, to the best of our knowledge, there is no work in literature systematically studying and comparing the linear and nonlinear viscoelastic properties of GO film at water/oil and water/air interfaces.

Hence, in chapter 7, to provide fundamental insight into the mechanical properties of the GO film at water/oil or water/air interfaces, we investigated linear and nonlinear interfacial viscoelastic response of water/air and water/oil in the presence of GO nanosheets by applying SAOS and LAOS flows at the interface using a du Noüy ring.\textsuperscript{65} These results pave the way for the development of new class of nanoparticle-stabilized emulsions of oil in water and open up opportunities to design new functional GO-based materials, e.g., bijels, which are rigid materials made up of two immiscible fluids held together by a jammed layer of nanoparticles.

1.6 Background

1.6.1 Parallel plates geometry

Figure 1-2a depicts the parallel-plate geometry. Parallel-plate geometry produces a linearly varying shear rate under a laminar flow. The shear rate is zero at the center point ($r=0$) and is $\gamma(R)=\Omega Rh$ at the sample edge ($r=R$). The apparent shear stress at the edge ($r=R$) can be calculated using the following equation:

$$\tau(R) = \frac{T}{2\pi R^2} (3 + \frac{d\ln T}{d\ln y(R)})$$  \hspace{1cm} (eq.1-1)

where $T$ is the torque applied by rheometer. It is required to measure the torque at various rotation speeds and plot of $T$ as function of $\gamma’ (R)$ to utilize the above equation.
The normal force $F_N$ measured by parallel-plate geometry yields the primary and secondary normal stress difference, expressed as:

$$N_1 - N_2 = \frac{F_N}{\pi R^2} \left( 2 + \frac{d\ln F_N}{d\ln \gamma(R)} \right)$$

\[eq.1-2\]

Figure 1-2: (a) parallel plates (typical gap-size = 0.1mm) and (b) cone and plate (typical gap-size = 0.05mm) geometries of rotational rheometers.

1.6.2 Cone and plate geometry

Cone-plate geometry features a small cone angle ($\alpha \leq 0.01$ rad). Based on this geometrical feature, the local shear rate experienced by the sample using a cone-plate geometry is independent of the radial, angular, and axial position. Under these conditions, the applied shear can be formulated by the following equation:

$$\dot{\gamma} \cong \Omega \alpha \ (for \ small \ \alpha)$$

\[eq.1-3\]

Hence the shear is only a function of cone angle and measuring device rotational speed ($\Omega$). The shear stress can also be simply calculated based on the applied torque ($T$) and cone radius ($R$).

$$\tau = \frac{3T}{2\pi R^3}$$

\[eq.1-4\]

By measuring the normal force $F_N$ exerted on the plate, it is possible to directly measure the primary normal stress difference ($N_1$).

$$N_1 = \frac{F_N}{\pi R^2}$$

\[eq.1-5\]
Typically, smaller sample size would be used in cone-plate geometry compared to parallel-plate geometry (this is due to the smaller gap-sizes of cone-plate geometry compared to parallel-plate geometry). Additionally, cone-plate is less prone to shear fracture due to much smaller free surface.

1.6.3 Small amplitude oscillatory shear (SAOS) rheometry.

The small amplitude oscillatory shear (SAOS) response of complex fluids can provide unique information on ultraslow relaxation process associated with structures formed by colloidal particles. The small amplitude sinusoidal strain ($\gamma$) is applied and within a few cycles upon start-up, the shear stress response ($\tau$) demonstrates sinusoidal oscillations at the same frequency ($\omega$) with a phase lag ($\delta$) with respect to the applied strain wave. The above descriptions can be formulated mathematically as follows.

\[
\gamma = \gamma_0 \sin \omega t \quad (eq.1-6)
\]

\[
\tau = \tau_0 \sin (\omega t + \delta) \quad (eq.1-7)
\]

Such an expression for stress wave can be decomposed into two waves of the same frequency, one term in-phase with the strain wave ($\sin \omega t$) and one term $90^\circ$ out-of-phase with the strain wave ($\cos \omega t$). Accordingly, it is possible to demonstrate mathematically that:

\[
\tau = G'\gamma_0 \sin \omega t + G''\gamma_0 \cos \omega t \quad (eq.1-8)
\]

\[
G^* = G'+G''i \quad (eq.1-9)
\]

\[
|G^*| = \tau_0/\gamma_0 \quad (eq.1-10)
\]

in which complex modulus ($G^*$), in-phase or elastic modulus ($G'$) and out-of-phase or loss modulus ($G''$) are dynamic moduli defined based on the decomposition procedure. The imaginary part $G''$ is a measure of energy dissipated per cycle of deformation per unit of sample volume.
1.6.4 Large amplitude oscillatory shear (LAOS) rheometry.

LAOS is a test method with growing popularity among researchers in the field. This test method is intended to highlight the onset of structural nonlinearities in complex fluids. The LAOS tests include oscillation cycles at multiple strain amplitudes.

Under LAOS flow, the sinusoidal input strain signal is transformed to a non-sinusoidal stress response. Different methods, such as Fourier transform rheology (FT-rheology) and stress decomposition, have been developed to analyze the non-sinusoidal stress response signals. For an oscillatory strain input \( \gamma(t) = \gamma_0 \sin(\omega t) \), the viscoelastic shear stress \( \sigma \) response at steady-state condition can be written as in-phase and out-of-phase components of a time-domain Fourier series of odd harmonics:

\[
\sigma(t) = \gamma_0 \sum_{n=1}^{N} [G'_n(\omega, \gamma_0) \sin n\omega t + G''_n(\omega, \gamma_0) \cos n\omega t]
\]

(\text{eq.1-11})

where \( \gamma_0 \) is strain amplitude, \( G'_n \) and \( G''_n \) are amplitudes of \( n \) harmonics with frequencies \( n\omega \). In the linear viscoelastic region, the output stress waveform is only a function of the first harmonic coefficient, \( n = 1 \). The excitation of higher harmonics in the output stress signal leads to emergence of nonlinearity in viscoelastic behavior of materials, meaning that the stress waveform cannot be described simply by sinusoidal waves. Moreover, in the nonlinear regime, \( G' \) and \( G'' \) have no longer a clear physical meaning, which means another method must be applied to interpret the stress signal.

FT-rheology is based on a sophisticated mathematical framework and is a powerful tool to detect nonlinearities and calculate higher order harmonics. However, it cannot give us a clear physical interpretation of the higher order harmonics and the ensuing nonlinear viscoelastic properties. In 2008, Ewoldt et al. proposed new nonlinear measures to interpret LAOS results.

Based on this approach, the stress response \( \sigma(t) \) can be decomposed into:
1) Elastic stress component (\(\sigma'\)) as an odd function of normalized strain \((x(t) = \frac{y(t)}{y_0})\).

2) Viscous stress component (\(\sigma''\)) as an odd function of normalized strain rate \((y(t) = \frac{\dot{y}(t)}{y_0})\). Thus, the total stress can be expressed as:

\[
\sigma(t) = \sigma'(t) + \sigma''(t).
\]  

\((eq.1-12)\)

A series of Chebyshev polynomials of the first kind\(^{39,68}\) in the orthogonal space formed by the input strain and strain-rate can be used to represent the elastic and viscous stress components via the following equations:

\[
\sigma'(x: \omega, \gamma_0) = y_0 \sum e_n(\omega, \gamma_0) T_n(x),
\]  

\((eq.1-13)\)

\[
\sigma''(x: \omega, \gamma_0) = \dot{y}_0 \sum v_n(\omega, \gamma_0) T_n(y)
\]  

\((eq.1-14)\)

where \(\bar{x} = \frac{x}{y_0}\) and \(\bar{y} = \frac{y}{y_0}\) represent normalized strain and strain-rate, and \(T_n\) represents Chebyshev polynomials. “\(e_\)” and “\(v_\)” are elastic and viscous contributions and have units of modulus (Pa) and viscosity (Pa.s\(^{-1}\)), respectively.

Using “\(e_\)” and “\(v_\)”, Ewoldt \textit{et al.}\(^{39}\) defined local viscoelastic moduli and viscosities. Comparison of nonlinear local viscoelastic moduli (\(G'_M\) and \(G'_L\)) and dynamic viscosities (\(\eta'_M\) and \(\eta'_L\)) can give us good insight into the type of intra-cycle nonlinear behavior. In each cycle of oscillation, large-strain modulus (\(G'_L\)) is measured at the point where deformation is maximum \((\gamma = \gamma_0)\), and minimum-strain modulus (\(G'_M\)) is measured at the point where deformation takes a zero value \((\gamma = 0)\). Both \(G'_M\) and \(G'_L\) converge to linear elastic modulus in small strain amplitude region, i.e., \(G'_M = G'_L = G'\).\(^{39}\) These elastic measures have been used by Ewoldt \textit{et al.}\(^{69}\) to develop a dimensionless index for interpretation of intra-cycle elastic nonlinearity defined as:

\[
S = \frac{G'_L - G'_M}{G'_L}.
\]  

\((eq.1-15)\)
\( S \) (strain stiffening ratio) value equal to 0 corresponds to linear viscoelastic response, a positive \( S \) indicates intra-cycle strain-stiffening behavior, and a negative \( S \) is indicative of intra-cycle strain-softening. Similar to the above-mentioned elastic measures, viscous parameters have been introduced to characterize intra-cycle viscous nonlinearity. In this context, a set of local dynamic viscosities have been defined as minimum-rate dynamic viscosity \( \frac{d\tau}{d\gamma}\bigg|_{\gamma=0} \equiv \eta'_M \) and large-rate dynamic viscosity \( \frac{d\tau}{d\gamma}\bigg|_{\gamma=\pm\gamma_0} \equiv \eta'_L \). \(^{39,69}\) Similar to the elastic measures, in the linear regime, dynamic viscosities converge to the linear real viscosity value \( \eta' = \frac{G'}{\omega} \), i.e., \( \eta'_L = \eta'_M = \eta' \). The dimensionless index for dissipative (viscous) intra-cycle nonlinearity has been proposed as:

\[
T = \frac{\eta'_L - \eta'_M}{\eta'_L}.
\]

(\textit{eq}.1-16)

\( T=0 \) signifies linearity, \( T>0 \) implies intra-cycle shear-thickening, and \( T<0 \) corresponds to intra-cycle shear-thinning.

Hence, in this thesis we investigate the nonlinearity of a wide range of viscoelastic materials using the mentioned method. It is anticipated that these data will provide much more insight into the microstructure complex fluids. Chapter 2 provides an overview of the materials and methods used in this thesis, and is followed by several chapters, each of which is a manuscript that has been published or will soon be submitted for publication. Finally, in Chapter 8, we provide conclusions and recommendations for future work. The key findings from this thesis are expected to give insight into investigation into structure of multiphase materials subjected to real conditions.

### 1.7 References


Chapter 2 - Materials, Processing and Characterization

2.1 Methodology and Chapters’ Overview

The main focus of the present Ph.D. dissertation is to link macro-scale nonlinear mechanical properties polymeric materials to their nano-scale structural features. To do this, we report nonlinear viscoelastic behavior of a wide range of viscoelastic systems under LAOS flow. In this chapter, we give an overview of the materials used, methods employed and a summary of the characterization methods. Results of this work were categorized into five phases presented in the following order:

(i) “Structural Characterization of CVD Custom-Synthesized Carbon Nanotube/Polymer Nanocomposites in Large-Amplitude Oscillatory Shear (LAOS) Mode: Effect of Dispersion Characteristics in Confined Geometries” in which for the first time I investigated the effect of physical features of CNTs (e.g., length, diameter, etc.) on nonlinear viscoelastic response of CNT-based polymer nanocomposites. Moreover, I showcased the effect of confinement of nanotubes’ clusters on LAOS response of CNT-based polymer nanocomposites. Chapter 3.

(ii) “Application of nonlinear rheology to assess the effect of secondary nanofiller on network structure of hybrid polymer nanocomposites” for which I studied the effect of addition of secondary nanofiller on network structure of CNTs in a polymeric media employing LAOS. Chapter 4.

(iii) “The key role of processing in tuning nonlinear viscoelastic properties and microwave absorption in CNT-based polymer nanocomposites” in which I investigated the effect of different types of mixing methods on network formation of CNTs from a rheological point of view. Chapter 5.
“On the viscoelastic response of covalently cross-linked gelatin methacryloyl (GelMA) hydrogel under large shear deformations” in which to mimic practical conditions and to evaluate the mechanical response of the hydrogels subjected to large deformations, I reported inter- and intra-cycle nonlinear viscoelastic behavior of GelMA with different concentrations of the hydrogel precursor (10 to 20% (w/v)) under LAOS deformation. To achieve this, we propose a novel technique by chemically bonding the hydrogels to treated glass-slides which are attached to the oscillating metal plates using a double-sided tape to alleviate any error arising from wall-slip in rheological measurements. Chapter 6.

“Outstanding interfacial viscoelasticity of graphene oxide at water/air and water/oil interfaces: a comparative study” in which the linear and nonlinear viscoelastic response of water/air and water/oil interfaces in the presence of the graphene oxide nanosheets were investigated employing SAOS and LAOS flows. Chapter 7.

2.2 Materials

2.2.1 Poly(vinylidene Fluoride) (PVDF)

Poly (vinylidene fluoride) (PVDF) is a semi-crystalline fluoropolymer with high chemical and heat resistance. PVDF 11008/0001 was purchased from 3M™ Canada and was used as the matrix for phase (i) and phase (ii) of this work. This PVDF has melt flow index of 24g/10min and melting point of 160°C with an average density of 1.78g/cm³.

2.2.2 Polystyrene (PS)

Polystyrene (PS) is an amorphous polymer. PS Styron 666D from Americas Styrenic LLC was used as matrix in Phase (iii). Due to excellent properties of PS (e.g., low price, transparency,
chemical resistance, etc.), it has application in packaging, consumer goods, electronic, and automobile industries.

### 2.2.3 Alumina

Alumina purchased from Sasol (γ − Al₂O₃, SBA 200 Catalox®) served as a substrate for CVD catalyst. It has average particle size of 45μm and a surface area of 90-210m²/g.

### 2.2.4 Gaseous reagents

Compressed Argon (>99.998%), Ethane (> 99%), and Hydrogen (>99.95%) gases were purchased from Praxair, Canada.

### 2.2.5 Iron (III) Nitrate Nonahydrate (Fe(NO₃)₃.9H₂O)

Iron (III) nitrate nonahydrate was purchased from J.T. Baker, Canada with ACS reagent specification. This white powder was used as a catalyst precursor in phase (i).

### 2.2.6 Multi-walled carbon nanotubes (MWCNTs)

In phase (i), CNTs were synthesized over the prepared catalyst (support alumina is impregnated with Iron (III) nitrite solution with the ratio of 20/80 between the catalyst and support) by chemical vapor deposition method (CVD) method at a broad spectrum of temperatures, i.e. 550 to 950°C (at 100°C intervals). CNTs synthesis time was fixed at 2h and the gas flow rates were 50/50/50sccm for ethane/argon/hydrogen. Catalyst mass was 0.6g.

In phase (ii) and (iii) MWCNT was acquired from Nanocyl S. A. (Sambreville Belgium) and the grade that used in this work is Nanocyl™ 7000. According to the manufacturer, Nanocyl 7000 was produced by CVD method. Average diameter of NC 7000 is 9.5nm, average length is 1.5μm, carbon purity is 90%, surface area is 250-300m²/g, and electrical conductivity is 10⁴-10⁵S/cm, according to manufacturer.
2.2.7 Methacrylic anhydride

In order to prepare GelMA hydrogel in Phase (iv), methacrylic anhydride (Aldrich 276685 94%) was purchased from Sigma-Aldrich.

2.2.8 Irgacure 2959

Irgacure 2959 was used as photo initiator for photo cross-linking of GelMA hydrogels in Phase (iv).

2.2.9 Oil phase.

Silicone oil (5cSt, Clearco #63148-62-9) was used as the oil phase in chapter 7, Phase (v).

2.2.10 Graphene oxide (GO) synthesize.

Natural graphite flake was used in order to synthesize GO. Graphite powder (Asbury Carbon, Natural flake) and sodium nitrate (2:1 ratio) (Sigma Aldrich, ReagentPlus®, ≥ 99%) were mixed with concentrated sulfuric acid in an ice bath. In the next step, the suspension was gradually mixed with potassium permanganate (3:1, KMnO₄: graphite) (Anachemia, Reagent Grade, 99%) under intense stirring and the temperature was kept under 20°C. Subsequently, the mixture was vigorously stirred at 35°C. The reaction was completed by formation of a brownish pasty mixture formed. This brownish pasty mixture was then diluted with deionized water in an ice bath to keep the temperature lower than 50°C. Afterwards, a solution of deionized water mixed with hydrogen peroxide (Sigma Aldrich, Reagent Grade, 30%) was added to the suspension and then stirred for 2h. After separation via centrifugation, the solids were washed using an aqueous solution contacting HCl to eliminate any residual ions. The graphite oxide was again rinsed with DI water. The obtained graphite oxide was exfoliated in water using a bath sonicator. The dispersed graphite oxide was centrifuged at 4000rpm to separate large unexfoliated solids.
2.3 Sample preparation

2.3.1 Phase (i)
PVDF matrix was melt-mixed with various CNT concentrations, i.e., 0.3, 0.5, 1.0, 2.0, and 2.7 wt.%, at 240°C and 235 rpm using APAM (Alberta Polymer Asymmetric Minimixer) mixer. The PVDF matrix was first masticated within the mixing chamber for 3 min, and then CNTs were introduced and mixed for an additional 14 min. A Carver compression molder (Carver Inc., Wabash, IN) was used to make disc-shaped samples at 220°C and 38 MPa for 10 min. The diameter and thickness of the samples were 25 mm and 0.5 mm, respectively.

2.3.2 Phase (ii)
PVDF/CNT and PVDF/MnO₂NW, and also hybrid nanocomposites (two-fillers), PVDF/CNT/MnO₂NW, were fabricated by melt mixing using APAM mixer at 240°C and 235 rpm. PVDF/CNT and PVDF/MnO₂NW were melt-mixed at four different total concentration of nanofillers, namely 0.5, 1.0, 1.5 and 2.0 wt.%, for 15 min mixing after initial 3 min mastication of PVDF alone. Hybrid PVDF/CNT/MnO₂NW nanocomposites were prepared at different MnO₂NW/CNT weight ratios (1 and 2) by mixing PVDF and CNTs for 7 min following by addition and mixing of MnO₂NW for 8 min. Nanocomposites were molded into circular disks (25 mm diameter, 0.2 mm thickness) with a Carver compression molder (Carver Inc., Wabash, IN) at 240°C under 35 MPa pressure for 10 min.

2.3.3 Phase (iii)
PS/MWCNT nanocomposites were prepared at different MWCNT loadings (0.3, 0.5, 1, 2, and 2.7 vol.%) using different mixing methods (solution mixing and melt mixing). During solution mixing, PS was dissolved in chloroform by 30 min of magnetic stirring and MWCNT was dispersed in chloroform by 30 min of bath sonication. Both of the mixtures were mixed and homogenized for
30min. After evaporation of the solvent, PS/MWCNT was dried in vacuum dryer. Melt-mixed PS/MWCNT samples were prepared at 230°C and 150rpm in Alberta Polymer Asymmetric minimixer (APAM). The samples were compression molded in Carver compression molder (Carver Inc. Wabash. IN) in a rectangular shape (10 x 23 x 0.8mm³) at 230°C. Pressure was maintained at 35MPa for 10min.

2.3.4 Phase (iv)

Gelatin powder was first dissolved in phosphate buffered saline (PBS) (pH 7.4) in 10% (w/v). While the solution was vigorously stirred at 50°C, 0.6g of methacrylic anhydride (Aldrich 27668 94%) for each gram of gelatin was added in a drop wise manner over a 3hr period. Then, pre-warmed PBS was used to quench the methacrylation reaction. Afterwards, in order to remove impurities, the solution was dialyzed for 4 days against ultra-pure DI water using a 12-14 KD filter. Then, the solution was snap-frozen in liquid nitrogen. The product was lyophilized in a freeze dryer for 5day. GelMA hydrogel was prepared by dissolving GelMA precursor in warm PBS at 10, 15, and 20%(w/v) concentrations. To initiate cross-linking under UV exposure (254nm, 10mW/cm², and 2min), a water-soluble photo-initiator (Irgacure 2959) was used (5mg/mL).

2.4 Characterizations

2.4.1 Compression molding.

A compression molding method was used to prepare samples for rheological and electrical characterizations. The setup includes two heated plates. Heating is necessary to melt the samples to attain the flow required to give them a particular shape. After elevating the temperature to the desired temperature, nanocomposite samples were kept in the mold for few minutes to melt the polymer and then the samples were kept under high pressure to get the desired shape.
2.4.2 Transmission electron microscope (TEM) imaging.
Dispersion of CNTs inside polymer matrix, size distribution of CNTs and MnO₂NWs was investigated by TEM. Tecnai TF20 G2 FEG-TEM (FEI, Hillsboro, OR) was used to capture TEM images.

2.4.3 Light microscope (LM) imaging.
An Olympus microscope BH2 equipped with a CCD camera DP71 (both from Olympus Deutschland GmbH, Hamburg, Germany) was used to capture images with dimensions of 600 × 800μm² from different cut sections. Thin sections were acquired at ambient temperature using Leica® EM UC6 (Leica Biosystems, Germany) ultramicrotome. Stream Motion (Olympus) and ImageJ are used to capture the images and further analysis.

2.4.4 Scanning electron microscopy (SEM) imaging.
The morphology of synthesized CNTs was observed using a scanning electron microscopy (SEM) setup, Philips XL30.

2.4.5 Broadband electrical conductivity.
In Phase (i), the broadband electrical conductivity of polymer nanocomposites was measured using a Bio-Logic impedance / gain-phase analyzer (SP-200 EIS) in the frequency range of 10² – 10⁶Hz. A 12962A sample holder with electrode diameter of 10mm was used for dielectric spectroscopy. Prior to the measurements, the electrodes were painted on the samples with a silver paste to reduce the effect contact resistance with sample holder electrodes.

2.4.6 Electromagnetic interference (EMI) Shielding.
All the EMI measurements was carried out by WR-90 rectangular waveguide using an Agilent programmable network analyzer (ENA) (Model E5071C). The network analyzer consists of a
signal source (which generates a single frequency signal to the sample), a receiver (which detects how much of the incident wave is reflected and transmitted by the sample), and a display.

2.4.7 Bulk and interfacial rheology.

Rheological measurements at elevated temperature were performed under a nitrogen atmosphere to reduce degradation of polymer chains using an Anton-Paar MCR 302 rheometer equipped with a 25 mm cone-plate geometry (a cone angle of 1° and a truncation of 47μm) or a 25mm parallel-plate geometry. The gap-size of parallel-plate geometry were fixed based on the thickness of the samples in each chapter. All experiments were carried out at 240°C for PVDF, 220°C for PS, and room temperature for GelMA hydrogels. Time sweep SAOS measurements at high temperature were performed on PVDF and PS confirming that no degradation of the samples occurred after the long time exposure at elevated temperatures. Linear and nonlinear regions were distinguished using strain amplitude sweep experiment. This test was done over a range of applied strain amplitudes from 0.1 to 1000% at a fixed angular frequency.

To obtain the large amplitude oscillatory shear (LAOS) results, the rheometer was placed in a rigid and mechanically stable environment to minimize any mechanical noise. To obtain last full waveform of shear stress and strain, the material was strained at a constant frequency and a constant amplitude. LAOS data were collected after 5-6 cycle for each strain amplitude.

The rheological tests at the interface of the aqueous nanofluids-oil were conducted using a DHR-3 rheometer from TA instruments equipped with a du Noüy interfacial geometry. In each experiment, the Teflon vessel is cleaned using wipes soaked in chloroform and dried with clean wipes and dry air. The Du Noüy ring is cleaned by soaking into chloroform, then fired to remove any residue, and allowed to cool down to room temperature. To study the interfacial viscoelasticity,
strain amplitude sweep (at angular frequency of $\omega = 1\text{rad/s}$) and time sweep tests (at $\omega = 0.5\text{rad/s}$, and strain amplitudes of $\gamma_0 = 0.1\%$) were performed on all samples at ambient temperature.

2.4.8 Interfacial tension.

Interfacial tension at water/air or water/oil interfaces has been measured using Wilhelmy plate coupled to an electrobalance (KSV Nima, Finland).

In summary, a wide range of characterization techniques were used to confirm the obtained linear and nonlinear results of the studied complex fluids in this thesis. These results verify that nonlinear rheology can be used as a powerful tool to investigate the network structure of the CNT-based polymer nanocomposites, hydrogels, and interfaces. Additionally, it was shown that intra-cycle viscoelastic parameters are extremely sensitive to subtle changes in the microstructure. Hence, this thesis provides further guidance for interpretation of the nonlinear response of the complex fluids.
Chapter 3 - Structural Characterization of CVD Custom-Synthesized Carbon Nanotube/Polymer Nanocomposites in Large Amplitude Oscillatory Shear (LAOS) Mode: Effect of Dispersion Characteristics in Confined Geometries **

Presentation of the Article:

This article is concerned with comparing the linear and nonlinear rheological properties of CNT-based polymer nanocomposites containing CNTs with different physical structures. To achieve this, we synthesized CNTs with different lengths and diameters using chemical vapor deposition method. Results reveal that physical features of CNT greatly affect dispersion state of the CNTs in the bulk of the polymer, which, in turn, impact the viscoelasticity of the nanocomposite samples. For instance, poorly-dispersed samples followed a multi-step yielding upon transition into nonlinear region, while, well dispersed systems showed a smooth single step transition. In addition to study the nonlinear behavior of the samples, for the first time we investigated the effect of confinement of the nanotube aggregates on viscoelastic response of polymer nanocomposites in MAOS and LAOS regions. To the best of our knowledge, this study is the first study in the area investigating the effect of physical properties of CNT on LAOS behavior of polymer nanocomposites.

Authors’ contributions:

I organized and wrote the paper. I performed rheological tests. Dr. Sadeghi helped with running rheological tests and with analyzing the rheological data. Dr. Arjmand helped with synthesize and characterization of nanotubes. He also helped in preparation of polymer nanocomposites. Prof. Sundararaj supervised the whole study.

** Macromolecules 52.4 (2019): 1489-1504, doi.org/10.1021/acs.macromol.8b01774
Structural Characterization of CVD Custom-Synthesized Carbon Nanotube/Polymer Nanocomposites in Large Amplitude Oscillatory Shear (LAOS) Mode: Effect of Dispersion Characteristics in Confined Geometries

Milad Kamkar\textsuperscript{a}, Soheil Sadeghi\textsuperscript{a}, Mohammad Arjmand\textsuperscript{b}, Uttandaraman Sundararaj\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a} Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr NW, Calgary, Canada T2N 1N4
\textsuperscript{b} School of Engineering, University of British Columbia, Kelowna, BC, Canada V1V 1V7
*Corresponding Authors: E-mail: u.sundararaj@ucalgary.ca (Uttandaraman Sundararaj)

For Table of Contents use only

3.1 Abstract

Poly(vinylidene fluoride) (PVDF) was melt-mixed with custom-synthesized multi-walled carbon nanotubes (CNTs) at various loadings to create polymer nanocomposites for electrical applications. The custom-made CNTs were fine tuned using chemical vapor deposition technique over a broad range of temperatures, i.e., from 550°C to 950°C at 100°C intervals. Characterization revealed that synthesis temperature had a huge impact on the structural features of CNTs and, consequently, on CNT network formation within the polymeric matrix. Oscillatory amplitude sweep test indicated that nanocomposites with poor conductive network showed a multi-step yielding in the nonlinear regime; i.e., storage modulus dropped to an intermediate plateau and then decreased significantly. Conversely, PVDF/CNT\textsubscript{650} (CNT synthesized at 650°C) nanocomposite with the highest conductivity, demonstrated a gradual single-step yielding process. Physical interpretations and structure-property relationships were expounded based on intra- and inter-cycle quantitative nonlinear viscoelastic parameters, which showed strongly dissipative nonlinearity at intermediate deformations for poorly conductive nanocomposites (PVDF/CNT\textsubscript{850} and PVDF/CNT\textsubscript{950}). Multiple gap-size rheometry of the nanocomposites confirmed that the dissipative feature of poorly-dispersed polymer nanocomposites originates from disruption of the bridges of nanofillers spanning the rheometer gap, i.e., aggregated structures experiencing rheometer plates confinement effect. Moreover, for the first time, we showcased the effect of confinement of nanofiller aggregates on intra-cycle viscoelastic response of polymer nanocomposites in both medium and large amplitude oscillatory shear regions.
3.2 Introduction

Microstructure of carbon nanotube (CNT) network in a polymer matrix affects the final properties of CNT-polymer nanocomposites (CPNs) and is established by multiple factors, such as molecular and physical features of CNTs, and CNT concentration and dispersion state within the polymer matrix.\textsuperscript{1-3} An extensive literature exists on the effect of physical features and dispersion state of CNTs on final properties of CPNs.\textsuperscript{4-6} For instance, Li et al.\textsuperscript{4} and Wu et al.\textsuperscript{7} claimed that CPNs containing CNTs with higher aspect ratio exhibited superior electrical, mechanical, and rheological features. In another study, Cipiriano et al.\textsuperscript{8} studied polystyrene/CNT nanocomposites with a focus on the effect of CNT aspect ratio and the resulting dispersion state on rheological properties. They observed that nanocomposites containing CNTs with large aspect ratio exhibited much higher storage modulus and shear viscosity compared to CPNs with lower aspect ratio CNTs. A similar trend was observed for the dielectric constant value\textsuperscript{9} and electromagnetic shielding effectiveness\textsuperscript{10} of CPNs.

Melt rheological response is an indirect method but is a strong indicator of the dispersion state and microstructure of the nanofillers in the bulk of a filled system.\textsuperscript{2,11-13} Many research studies have been carried out on the structure-property relationships for various CPN systems using linear viscoelastic data obtained under small amplitude oscillatory shear (SAOS) flow.\textsuperscript{14} Although SAOS tests provide useful information about the relationship between the microstructure and rheological properties, it should be borne in mind that SAOS flow is limited to a narrow strain or stress region. Therefore, rheological measurement under intermediate and large strain amplitudes have the potential to reveal important additional and complementary information regarding new aspects of materials response not accessible via linear rheology. Moreover, since SAOS tests evaluate the viscoelastic behavior of the complex fluids under small strain amplitudes, these tests might be
unable to distinguish complex fluids with similar nano or molecular structures, but may show different nonlinear rheological behavior.\textsuperscript{15} Thus, the SAOS-based analysis methods are not adequate to fully understand the nano or molecular structure of polymer nanocomposites,\textsuperscript{16} so an in-depth investigation of the nonlinear behavior of CPNs is necessary.

Given the limitations of SAOS, and to simulate large-deformation industrial processing conditions, large amplitude oscillatory shear (LAOS) flow has drawn great interest. Additionally, as the strain amplitude and frequency can be controlled independently, LAOS flow covers a wide spectrum of nonlinear situations with respect to time and deformation.\textsuperscript{17-18} Considering the aforementioned reasons, over the last decade, LAOS has been extensively employed to study nonlinear viscoelasticity to detect any changes in topology, morphology, concentration, etc. in a variety of systems, such as polymer solutions,\textsuperscript{19-20} polymer nanocomposites,\textsuperscript{21} and polymer hydrogels.\textsuperscript{22} LAOS approach provides an extensive framework to detect intra-cycle nonlinearities, providing vital information for the structure-property relationship of the filler-polymer systems. For instance, Lim et al.\textsuperscript{23} investigated the nonlinear response of polymer nanocomposites filled with differently shaped nanoparticles under LAOS flow, and they quantified the nonlinear flow response using stress decomposition and FT-rheology methods. They reported different values for the third harmonic ratio ($I_3/1$) as nanoparticles’ shape changes, suggesting that nonlinear parameters can be used to delineate the internal structure of polymer nanocomposites. In another study, Hyun et al.\textsuperscript{24} investigated the viscoelastic behavior of a polymer composite system using LAOS flow. Their study revealed that nonlinear viscoelastic parameters are sensitive to polymer composite morphology, making it a useful technique in the assessment of dispersion quality or internal structures. The authors also demonstrated that nonlinear rheological data obtained under LAOS
flow are useful to magnify small differences in nanofillers structural evolution, inaccessible to linear rheology methods.

To the best of our knowledge, there is no study in the literature systematically investigating the effects of the physical and molecular structure of carbon nanotubes on the nonlinear viscoelastic behavior of CPNs under LAOS flow. Accordingly, using nonlinear viscoelastic rheological response, this work provides an in-depth understanding and a detailed explanation on the microstructure of CPNs filled with CNTs having distinct physical and structural features. To achieve this, we synthesized different types of CNTs and manipulated their structure (length, diameter, carbon purity, crystallinity, etc.) by changing the synthesis temperature in a chemical vapor deposition (CVD) process. Our previous study\textsuperscript{25} revealed that the synthesis temperature has a considerable impact on the morphological and molecular features of CNTs. This provided a unique substrate to investigate the impact of CNT structure on network formation behavior from a rheological point of view. We used optical microscopy and broadband AC conductivity to verify the rheological observations.

3.3 Experimental

3.3.1 Materials synthesis and characterization.

A detailed description of the CNT synthesis conditions, nanocomposite preparation, and CNT and nanocomposite characterizations is provided elsewhere.\textsuperscript{25} Here we summarized CNT synthesis and nanocomposite preparation. Employing chemical vapor deposition (CVD) technique, CNTs were synthesized over Fe catalyst/alumina substrate (20:80wt\%) at different temperatures, i.e., 550°C to 950°C (at 100°C intervals). Ethane was used as the gas precursor, whereas argon and hydrogen played the role of the gas carrier. The polymer matrix for nanocomposite was polyvinylidene fluoride (PVDF) 11008/0001, 3M Canada, with a melting point of 160°C. Molecular weight
averages of this PVDF grade are reported as $M_n = 43000$ (g mol$^{-1}$), $M_w = 117000$ (g mol$^{-1}$), and $M_z = 259000$ (g mol$^{-1}$) by the supplier. The zero-shear viscosity and the longest relaxation time of this PVDF matrix are estimated as 2.1kPa.s and 10.3s based on a creep-recovery experiment at $240^\circ$C, a shear-stress of 50Pa, a creep time of $10^4$s, and a recovery time of 2000s. The observed value of longest relaxation time indicates that ultraslow relaxation modes introduced by the presence of CNTs network structure will not be masked by the PVDF matrix relaxation process.

The APAM$^{26}$ (Alberta Polymer Asymmetric Minimizer) mixer was used to melt-mix CNTs with the PVDF matrix at 240°C and 235rpm. The PVDF matrix was first masticated within the mixing chamber for 3min, and then CNTs were introduced and mixed for an additional 14min. For each synthesized CNT, nanocomposites with various CNT concentrations, i.e., 0.5, 1.0, 2.0, and 2.7wt%, were prepared. Nanocomposites were molded into circular disks (25mm diameter, 0.5mm thickness) with a Carver compression molder (Carver Inc., Wabash, IN) at 220°C under 38MPa pressure for 10min.

### 3.3.2 CNT characterization.

The carbon purity and structure of CNTs were examined with a Thermogravimetric Analyzer (TA Instruments, Model: Q500). CNTs were heated under air atmosphere from ambient temperature to 900°C at a ramp rate of 10°C/min. Morphology of synthesized CNTs was observed using a scanning electron microscopy (SEM) setup, Philips XL30. To measure the length and diameter of CNTs, a transmission electron microscopy (TEM) setup, Tecnai TF20 G2 FEG-TEM (FEI, Hillsboro, Oregon, USA) was employed. The measurement of the length and diameter was conducted for 150 individual CNTs. The conductivity of the compressed powders was measured at 90V using a Loresta GP resistivity meter (MCP-T610 model, Mitsubishi Chemical Co., Japan)
equipped with an ESP probe. Prior to the measurement, CNT powders were compressed into the circular mold using the Carver compression molder under 38MPa pressure for 10min.

3.3.3 Nanocomposite characterization.

The dispersion state of CNTs within the PVDF matrix was evaluated in two scales, microdispersion and nanodispersion, for nanocomposites with 2.0wt% loading. The microdispersion state of CNTs within the PVDF matrix was quantified using light microscopy (LM) employing an Olympus microscope BH2, in transmission mode. The observations were carried out on microtomed layers (5µm thickness) of the nanocomposites. Following the British Standard ISO 18553:2002 method, the agglomerate area ratio was calculated using the area covered by large agglomerates with sizes equal to, or larger than, a circle with a 5µm diameter (area: 19.6µm²) over the whole sample area. The calculations were performed for 15 different cuts, each with a surface area of 600×800µm². The relative transparency was calculated by dividing the transparency of the sample embedded between a glass slide and cover glass over the transparency of the glass slide/cover glass assembly.

3.3.4 Broadband electrical conductivity.

The broadband electrical conductivity of the nanocomposites was measured with a Bio-Logic Impedance Analyzer (SP-200 EIS) in the frequency range of 10² to 10⁶Hz, as per ASTM D150. The impedance analyzer was coupled with a Solartron 12962 sample holder with an electrode diameter of 10mm. The amplitude of the applied voltage was 100mV (Vrms ~ 70mV). Prior to the measurements, the electrodes were painted on the samples using silver paste.
3.3.5 Rheology.

The rheological behavior was evaluated using a strain-controlled rheometer (MCR 302, Anton Paar) equipped with a 25mm cone-plate geometry (a cone angle of 1° and a truncation of 47μm) and a 25mm parallel-plate geometry at 240°C. In order to determine the origin of nonlinearity in neat polymer and filled systems with CNTs, large amplitude oscillatory shear (LAOS) tests were conducted on neat PVDF and CNT/PVDF nanocomposites. In this regard, quantitative nonlinear parameters, such as intra-cycle nonlinearities conjugated with qualitative analysis of Lissajous-Bowditch plots, were used to evaluate the nanofiller network structure through the polymer medium. Rheological tests were carried out on triplicates and quadruplicates for each synthesized CNT, and the average results are presented in this paper. To confirm the negligible impact of inertial effects originating from the polymer melt sample and the instrument, we have estimated the onset of sample/instrument inertial effects and have co-plotted them with our measurements for the neat PVDF melt in Figure S1 of Appendix A. The details of these calculations can be found in a published work by Ewoldt et al.27.

3.4 Results and discussion

3.4.1 Structural and morphological characterization of nanofillers and nanocomposites.

Plots in Figure 3-1 display the thermal features, length and diameter, powder conductivity, and quantified microdispersion state of synthesized CNTs within the PVDF matrix. Thermogravimetric analysis (TGA) data and its first time derivative (DTG) were used to obtain information about carbon purity, crystallinity, and quality of synthesized CNTs (Figures 3-1(a-c)). In the TGA, the amount of the degraded material represents carbon purity, and the residue after thermal degradation represents catalyst particles. TGA results indicated that CNTs synthesized at 550°C, 650°C, 750°C, 850°C and 950°C had carbon purities of ~ 43, 85, 73, 71, and 69%,
respectively. These results reveal that 650°C is the optimum temperature to obtain high carbon purity. Inferior carbon purity at 550°C is due to low synthesis temperature, whereas low carbon purities at 750°C and higher can be related to the sintering of catalyst nanoparticles, which undermines catalyst surface, leading to the formation of carbonaceous material.²⁸

It was observed that the onset degradation point for CNT₅₅₀ was much lower than that of the other types of CNTs, attributed to amorphous carbon or defective CNTs.²⁹⁻³⁰ On the other hand, CNT₆₅₀ and CNT₇₅₀ presented narrow DTG curves, suggesting superior purity over the other CNTs. It should be noted that the carbon purity of CNT₇₅₀ is inferior to CNT₆₅₀, and is related to more sintering of catalyst particles at 750°C. CNT₈₅₀ and CNT₉₅₀ exhibited a very different shape of DTG curve in comparison to the other types of CNTs. This shape of thermogram denotes the significant amount of thermally resistant carbonaceous materials, in addition to CNT and catalyst.²⁵ We believe that the thermally resistant carbonaceous materials formed on the surface of large sintered catalyst particles or on the CNTs themselves, due to excessively high synthesis temperature. TEM images of CNTs, illustrated in our previous works, revealed that a thick carbonaceous layer deposited on the peripheral wall of the as-formed CNTs at 850°C and 950°C.²⁵,²⁸ Moreover, it was observed that CNTs synthesized at 850°C and 950°C had much higher crystallinity than the other types of CNTs, deduced from their high onset and inflection points.

Synthesized CNTs presented a broad range of length and diameter; accordingly, we performed statistical analysis of length and diameter for more than 150 individual CNTs for each sample and calculated the average length and diameter. Figure 3-1(d) depicts the length and diameter of CNTs synthesized at different temperatures. It was observed that all synthesized CNTs showed an average length of ~ 1.4µm; nevertheless, they showed very different diameters. CNTs synthesized
at 550°C, 650°C, and 750°C presented average diameter of 22, 15 and 29nm, respectively. CNTs synthesized at 850°C and 950°C showed very large average diameter of 80 and 95nm, respectively. CNT diameter is related to catalyst size, i.e., larger catalyst particles lead to larger CNT diameter. Therefore, the higher diameter of CNT\textsubscript{850} and CNT\textsubscript{950} is due to the larger size of catalyst particles formed due to sintering at high temperatures.\textsuperscript{28}

Synthesized CNTs displayed a very high powder conductivity (Figure 3-1(e)), endorsing the high quality of synthesized CNTs. It is worth noting that the conductivity of CNT powders had an ascending trend with the synthesis temperature, revealing the presence of amorphous carbon at low synthesis temperature (550°C) and the graphitic structure of thermally resistant carbonaceous materials at high synthesis temperatures (850°C and 950°C).
Figure 3-2 depicts the SEM images of CNT powders and schematics illustrating the effect of synthesis temperature on the formation of amorphous carbon, carbon nanotube, and thermally resistant carbonaceous materials. As demonstrated in Figure 3-2, the micrograph of CNT550 displays the highest density of catalyst particles among all samples (white arrows), covered by small-diameter CNTs; this is in accord with low carbon purity for CNT550. The micrograph for...
CNT$_{650}$ shows intense growth of tangled low-diameter CNTs over the catalyst particles. At higher synthesis temperatures, particularly 850°C and 950°C, CNTs with much larger diameters are visible, attributed to sintering of catalyst particles. SEM micrographs of CNT$_{850}$ and CNT$_{950}$ also show the formation of thermally resistant carbonaceous materials on the surface of large catalyst particle clusters (white arrows), as continued by TGA.

Figure 3-2: SEM micrographs and schematics illustrating the structure of carbonaceous materials formed at various synthesis temperatures. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society.

LM images of the microtomed CNT/PVDF nanocomposites with 2.0wt% loading are shown in Figure 3-3. To further clarify the dispersion state, schematics of dispersion state of formed carbonaceous materials within the PVDF matrix are illustrated in Figure 3-4. As shown in Figure 1(f) and Figure 3-3, nanocomposites with CNT$_{650}$ and CNT$_{750}$ had the lowest and highest
agglomerate area ratio, respectively, while the three other nanocomposites had intermediate values. Furthermore, the relative transparency in LM images qualitatively disclosed the quantity of agglomerates with sizes equal to or slightly larger than the wavelength of visible light (ca. 400-700nm) but smaller than visually perceptible agglomerates. Therefore, nanocomposites with the lowest transparency (highest darkness) would possess the highest density of agglomerates in the range of the wavelength of the light. The lowest relative transparency is seen for nanocomposites with CNT$_{650}$, that is, it is much darker than all other nanocomposites (see Figure 3-1(f)). The low transparency of the CNT$_{650}$/PVDF nanocomposite is thought to be related to low diameter and high quality and carbon purity of CNT$_{650}$. The nanocomposites with CNT$_{850}$ and CNT$_{950}$ showed, by far, higher transparency than the other nanocomposites. We ascribe this to the presence of large-diameter CNTs and thermally resistant carbonaceous materials, which have much less surface area than low-diameter CNTs, and thus may not be as well distributed in the matrix.

![Figure 3-3: LM images of microtomed CNT/PVDF nanocomposites with 2.0wt% CNT loading. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society.](image)

TEM was employed to characterize agglomerate sizes below the LM limit (nanodispersion), where individually dispersed CNT can be imaged. TEM images are presented in our former study, and showed that CNT$_{850}$ and CNT$_{950}$ nanocomposites have large agglomerates of sintered catalysts, and no individual CNTs were spotted. In line with LM, CNT$_{650}$ had the best nanodispersion, where individual CNTs were observed. In summary, it can be claimed the best
dispersion state was observed for CNT\textsubscript{650}/PVDF nanocomposites, while nanocomposites with CNT\textsubscript{850} and CNT\textsubscript{950} showed the worst dispersion state.

![Dispersion State Schematics](image.png)

**Figure 3-4**: Schematics depicting dispersion state and physical feature of CNTs synthesized at various temperatures within the PVDF matrix. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society.

### 3.4.2 Broadband electrical conductivity.

The broadband electrical conductivity is commonly denoted as \( \sigma = \sigma_{\text{DC}} + \sigma(\omega) \), where \( \omega \) is angular frequency; \( \sigma_{\text{DC}} \) is direct current (DC) conductivity, which is frequency independent and derives from the movement of free charge carriers in phase with the applied electric field; \( \sigma(\omega) \) is named alternating current (AC) conductivity and increases with frequency. AC conductivity originates from out-of-phase current and is created by the realignment of electric dipoles in each half cycle of the alternating field. In insulative materials, broadband electrical conductivity shows an ascending trend with frequency (AC conductivity prevails), whereas in conductive materials, broadband electrical conductivity is frequency independent (i.e., DC conductivity dominates). In semi-conductive materials, there is a critical frequency below which DC current prevails, while beyond this frequency, AC current is dominant.\(^{31-32}\) Accordingly, monitoring broadband electrical conductivity is a very powerful way to detect the level of conductive network formation in conductive filler/polymer nanocomposites.

Surprisingly it was observed that nanocomposites made with CNT\textsubscript{850} and CNT\textsubscript{950} showed an ascending trend with frequency for all the introduced CNT loadings, characteristic of an insulative
material (Figure 3-5). This implies that no conductive network was formed in these two nanocomposites, even at high CNT loadings. As already noted, powder conductivity of synthesized CNTs tracked with the synthesis temperature. Thus, the lack of conductive network formation in CNT_{850} and CNT_{950} nanocomposites can be attributed to CNT geometrical features or their dispersion state within the PVDF matrix. Using TGA, SEM, and TEM analyses, these CNT materials had intermediate carbon purity, large diameter, inferior quality, and presence of huge amount of thermally resistant carbonaceous materials on sintered catalyst particles. This coupled with poor microdispersion and nanodispersion state in their corresponding nanocomposites hindered the formation of the conductive network. Per excluded volume and statistical percolation theories,\textsuperscript{33-34} spherical particles have much higher percolation threshold than cylindrical particles, and the percolation threshold has an inverse power law relationship with the aspect ratio. This partially explains why large-diameter CNTs and carbonaceous materials formed on the surface of catalyst clusters at 850°C and 950°C could not form any conductive network.

Nanocomposites made with CNT_{550} and CNT_{750} showed an insulative behavior up to 2.0wt% CNT and were semi-conductive at 2.7wt%. The critical frequency for these two nanocomposites is shown by red arrows in Figure 3-5. Higher critical frequency observed for CNT_{750}/PVDF nanocomposites indicates that this nanocomposite has a better conductive network than CNT_{550}/PVDF nanocomposites. Higher critical frequency means that higher out-of-phase current due to electric dipole reorientation is needed to surpass the in-phase electrical current owing to free charge carriers.\textsuperscript{35} Nanocomposites made with CNT_{650} presented semi-conductive behavior at 0.5wt%, and conductive behavior at 1.0wt% and higher. This shows that the percolation threshold is about 0.5wt% for CNT_{650}/PVDF nanocomposites, much lower than the other nanocomposites. The differences in the broadband electrical conductivity of CNT_{550}, CNT_{650}, and CNT_{750}
nanocomposites are due to various factors, such as carbon purity, length and diameter of CNTs, crystallinity of CNTs, CNT dispersion state within the PVDF matrix, etc.\textsuperscript{36-37} The carbon purities for CNT\textsubscript{550}, CNT\textsubscript{650}, and CNT\textsubscript{750} were 43.6\%, 85.4\%, and 72.7\%, respectively. Hence, CNT\textsubscript{650} had a higher amount of CNTs per filler loading, whereas CNT\textsubscript{550} was mainly catalyst particles, which is not advantageous for conductive network formation. Theoretical and experimental studies report that well-dispersed CNTs with a higher aspect ratio (i.e., larger length and/or smaller diameter) provide enhanced conductive network formation.\textsuperscript{4} Smaller diameter means higher interacting surface area per mass of CNTs, and CNTs with larger length have more probability of touching each other. The superior electrical behavior of CNT\textsubscript{650}/PVDF nanocomposites can be related to high carbon purity, crystallinity, quality, small diameter, and good dispersion state of CNT\textsubscript{650} within the PVDF matrix. Comparing electrical conductivity of CNT\textsubscript{550} and CNT\textsubscript{750} nanocomposites shows that the higher carbon purity of CNT\textsubscript{750} overshadowed its higher agglomerate area ratio and larger diameter than CNT\textsubscript{550} as CNT\textsubscript{750} nanocomposites provided a slightly better conductive network. It is worth pointing out that the low electrical conductivity of the developed CPNs (10\textsuperscript{-2}S.m\textsuperscript{-1}) compared to individual metallic CNTs (10\textsuperscript{7}S.m\textsuperscript{-1}) can be attributed to: (1) extremely low concentration of CNT in the generated PVDF nanocomposites (0.5-2.7wt\%), (2) contact resistance between the CPNs and impedance spectrometer, and (3) the constriction resistance in low-concentration CPNs, due to the governing mechanisms of the electrical conduction-- these mechanisms include direct contact (metallic conduction), hopping, and tunneling.\textsuperscript{38} However, the electrical conductivity of our nanocomposites are comparable with electrical conductivity results in literature of similar composites.\textsuperscript{39-40}
Figure 3-5: Broadband electrical conductivity of nanocomposites containing CNTs synthesized at various temperatures. The critical frequency for CNT550 and CNT750 nanocomposites containing 2.7wt% of the nanofiller is shown by red arrows. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society.

3.4.3 Oscillatory frequency sweep.

We have demonstrated that synthesis temperature affects the structure, i.e., nanometric sizes, carbon purity, aspect ratio, and specific surface area, of CNTs. These differences in structural parameters result in dissimilar dispersion states and superstructures formed by the nanofillers within the polymer medium, leading to drastically different conductive networks. In this section, in order to provide further insights into the microstructures formed in CPNs, the well-established
An oscillatory frequency sweep test was used to study viscoelastic behavior. The observed viscoelastic responses were then correlated to the nanofiller network structures.

Figure 3-6 presents the frequency dependence of the storage modulus ($G'$) and loss modulus ($G''$) of CPNs containing 1.0wt% CNT measured at 240°C and three different strain amplitudes (1%, 10%, and 100%). It is known from the literature that network structures formed by anisometric fillers result in a yield stress behavior, which in turn leads to a low-frequency plateau-like pattern in $G'$ and $G''$. Generally, $G'$ shows more sensitivity to any changes in microstructure and the non-terminal behavior is more pronounced in $G'$ compared with $G''$ (see Figure 3-6).

The substantial differences in the observed frequency dependence of $G'$ reveal that the synthesis temperature had a tremendous impact on the nanocomposites rheological behavior. As can be seen in Figure 3-6(a), nanocomposite systems containing CNT_{550}, CNT_{850}, and CNT_{950}, with poorly-dispersed CNT structures and large agglomerates, had significantly higher $G'$ and exhibited a frequency-independent response, suggesting a solid-like behavior.
In line with our observation, Song et al.\textsuperscript{5} studied the effect of CNT dispersion in an epoxy resin on rheological, mechanical, electrical, and thermal properties. They achieved different dispersion states by manipulating the mixing method. Using a parallel-plate geometry at a gap-size of 1\,\text{mm} they showed that systems with poorly-dispersed CNTs have much higher storage modulus than those with well-dispersed CNTs. The poor dispersion state was considered as the origin of observing much higher storage modulus values and the intensified solid-like behavior.

In another study, Majumdar et al.\textsuperscript{41} investigated the rheological response of the flocculated multi-walled CNT (MWCNT) and carbon black suspensions at different gap-sizes in a parallel-
plate geometry. At a constant shear stress and a fixed MWCNT content, they reported a transition into a jammed rheological behavior as the gap-size decreases.

In fact, as shown in Figure 3-3, sintering of the catalyst particles at higher temperatures led to a huge increase in the size of the dispersed phase in CNT_{850} and CNT_{950}. These poorly-dispersed domains can form rheometer plates-spanning structures under confinement, intensifying the elastic response. In the cone-plate geometry used in this study, the truncation at the cone tip is 47.0μm and the gap-size increases to roughly 265μm at the edge of the loaded sample. The observed confinement effect manifests the existence of micron-sized clusters, well within the optical microscope resolution range, which can be identified with ease in the optical micrographs shown in Figure 3-3. Huang et al.\textsuperscript{42} have shown that samples with the cluster size of nanotubes comparable with rheometer plates gap-size would show erratic behavior, due to the wedging of the clusters between the plates. Analogously, observing a plateau in the storage modulus of CNT_{850} and CNT_{950} nanocomposites can be linked to a rheologically jammed state of clusters formed under confinement in these samples. Unlike the confined state in CNT_{850} and CNT_{950} nanocomposites, exhibiting a strong solid-like behavior signified by a frequency-independent storage modulus, for CPNs containing CNT_{650} and CNT_{750} a gradual decrease in the slope of $G'$ in the low-frequency region was observed. For CNT_{650}/PVDF and CNT_{750}/PVDF the nonterminal behavior indicates that carbon nanotubes either hindered or masked terminal relaxation process of the polymer chains in the nanocomposite systems. This behavior is a direct consequence of homogeneous dispersion state of the nanotubes in these nanocomposite samples.

To verify plates-spanning network formed by poorly-dispersed systems under confinement, the rheological properties of CNT_{950} with poor dispersion state (jammed structure) and CNT_{650} with a homogeneous dispersion state in the PVDF matrix were compared at several gap-sizes
of cone-plate and parallel-plate geometries (see Figure S3 and the related discussions in the Supporting Information, Appendix A).

Correspondingly, the $(\tan\delta)_{\text{max}}$ peak, observed at strain amplitude of 1%, shifted to higher frequencies for CNT$_{550}$, CNT$_{850}$ and CNT$_{950}$ nanocomposites, indicating a completely different microstructure compared to those formed by CNT$_{650}$ and CNT$_{750}$ (see Figure S2(a)). This peak in damping factor marks the transition from the short-time dynamics (controlled by polymer matrix) to the long-time dynamics (controlled by the nanofiller network structure). The sharp decrease in $\tan\delta$ value at low frequencies for CNT$_{550}$, CNT$_{850}$, and CNT$_{950}$ at the strain amplitude of 1% indicates a strong elastic behavior for these nanocomposites, in agreement with the previous results.

Figure 3-6(b) and 3-6(c) illustrate the $G'$ obtained at the strain amplitudes of 10% and 100% as a function of frequency. Wu et al.\textsuperscript{43} evaluated $G'$ of MWCNT/poly (butylene terephthalate) as a function of frequency for different strain amplitudes ranging from 1% to 50%. They observed a reduction in the value of the $G'$ with increasing strain amplitude. This was ascribed to a decrease in the number density of load-bearing points in the CNT network at higher strain amplitudes. The same trend was observed for our CPN samples. By increasing the strain amplitude, a large drop in $G'$ of CNT$_{550}$, CNT$_{850}$, and CNT$_{950}$ nanocomposites was observed, and the frequency dependence of the $G'$ dramatically increased. In contrast, only a slight change in storage modulus was seen for CNT$_{650}$ and CNT$_{750}$ nanocomposites. Particularly, at 100% strain, CNT$_{650}$ nanocomposite had the highest $G'$ value, whereas it was in the middle of the group for 1% strain.

Figure S4 in the Supporting Information (Appendix A) shows the results of strain amplitude sweep of PVDF nanocomposites containing CNT$_{650}$ and CNT$_{950}$ at various nanofillers loadings (for easier comparison, the storage modulus was normalized with respect to the plateau modulus). As can be seen, the critical strain amplitude (highlighted points with circle symbols),
where the samples exceed the limit of the linear viscoelastic regime, decreased for CNT_{650}/PVDF nanocomposites by increasing the loading of the nanofiller. Shih et al. proposed a scaling model relating the rheological properties of filled systems to particle concentration. Authors defined two distinct regimes, namely strong-link and weak-link regimes. In a strong-link regime, inter-floc links are stronger than the intra-floc links. They envisioned the gelation process and emergence of a solid-like rheological behavior in the frame of aggregating fractal flocs. In another study, Wu et al. proposed a scaling model to relate the structure of the colloidal gels to their elastic behavior. They used storage modulus and the limit of linearity of different systems to validate their rheological model. The authors defined the limit of the linearity as “the situation where the weakest bonds break and the linear elastic behavior vanishes”, and showed that by increasing the loading of the nanofillers the limit of the linearity increased for the weak-link regime and decreased for the strong-link regime. Therefore, based on the results shown in Figure S4 of Appendix A, we can classify CNT_{650}/PVDF nanocomposite as a strong-link gel.

In contrast, increment in the nanofiller concentration did not affect the critical strain amplitude of CNT_{950}/PVDF samples (see Figure S4 pf Appendix A, the first yielding strain amplitude remained intact and the second yielding occurred even at higher strain amplitudes by increasing the nanofiller content). Thus, we can classify CNT_{950}/PVDF samples as a weak-link gel. Hence, in systems with strong attraction potential and better state of nanofiller dispersion, we expect to have a higher number of strong inter-floc links between the flocculated structures forming a strong network. Thus, based on the above-described scheme, it could be concluded that the physical network formed by well-dispersed, strongly interacting CNT_{650} and CNT_{750} can survive up to the higher deformation levels, while the sparse, non-interacting agglomerates formed by poorly-dispersed nanotubes in CNT_{550}, CNT_{850}, and CNT_{950} based nanocomposites are less resilient to yielding. That is, CNT_{650} has the highest $G'$ at strain amplitude of 100%.
Correspondingly, as the strain amplitude increased, a shift in $\tan\delta$ peak toward lower frequencies is observable (see Figure S2 of Appendix A). This shift implies the disappearance of the solid-like response and yielding in these samples.

These results are consistent with optical micrographs (Figure 3-3) and transmission electron micrographs from our previous study, suggesting that agglomerates in CNT$\text{_{550}}$, CNT$\text{_{850}}$, and CNT$\text{_{950}}$ nanocomposites are isolated, and no effective nano-scale dispersion was achieved in these systems. For CNT$\text{_{650}}$ and CNT$\text{_{750}}$ based nanocomposites, effects such as a higher effective surface area and shorter distance between nanofiller domains may improve reinforcement effect of the CNTs network in the polymer matrix, leading to less sensitivity of elastic response to the deformation amplitude.

Comparing storage modulus of CNT$\text{_{650}}$/PVDF and CNT$\text{_{750}}$/PVDF at different strain amplitudes suggests a better network structure for CNT$\text{_{650}}$. This is due to the higher carbon purity and better physical dimensions (e.g., aspect ratio) of the CNT$\text{_{650}}$. These features of CNT$\text{_{650}}$ resulted in a higher number of individually dispersed CNTs in CNT$\text{_{650}}$/PVDF nanocomposite and, thus, higher CNT-polymer interfacial surface area, leading to a higher increase in $G'$ due to CNTs reinforcement effect. The same conclusion can be drawn based on the $\tan\delta$ graphs (Figure S2 of Appendix A). CNT$\text{_{650}}$ has a lower value in (tan$\delta$)$_{\text{max}}$; i.e., the more pronounced hindering effect on the polymer chains occurs due to the presence of a higher number of dispersed CNTs.

3.4.4 Strain amplitude sweep (inter-cycle viscoelastic behavior).

Figure 3-7 shows the strain sweep results for neat PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes (strain amplitude range is 0.1 to 1000% at an angular frequency of 10rad/s). For easier comparison, the dynamic moduli were normalized with respect to their maximum values (these values are tabulated in Table S1 of the Supporting Information (Appendix A)). Only 1.0wt% data is shown because the same behavior was observed for other samples containing 0.3, 0.5, 2.0 and 2.7wt% CNTs (see Figures S4 and S6
of Appendix A). The neat PVDF showed a dramatic drop in $G'$ as the strain amplitude increases and the transition from linear regime to nonlinear regime took place. This behavior, which is a typical behavior of highly entangled polymer melts, is a result of the dissociation of the entanglements and orientation of chains with the flow direction, which leads to local drag reduction.46

As can be seen in Figure 3-7, for all nanocomposites, except CNT$_{650}$/PVDF, there is a multi-step yielding as the strain amplitude exceed the limit of linear viscoelasticity. The multi-step transition has been observed for a number of systems due to different underlying mechanisms.47-48 To better describe the nonlinear behavior in our systems, we defined four different regimes at their corresponding strain amplitude regions. The first regime (i), where $G'$ is almost independent of the imposed strain amplitude, corresponds to the linear viscoelastic region (LVR). In the second regime (ii), $G'$ decreased into an intermediate plateau (third regime (iii)), and in the last regime (iv) there is a dramatic decrease in $G'$. The first drop in elasticity in the second regime (ii) was accompanied by a local peak in $G''$, for CNT$_{950}$/PVDF (see the insets for CNT$_{850}$/PVDF and CNT$_{550}$/PVDF). The local peak in $G''$ of elastomers is known as “Payne effect”, which is due to bond breaking between load-bearing points.49 This behavior reveals a dissipation process at intermediate strains for nanocomposites with poor state of dispersion.
Figure 3-7: Oscillatory amplitude sweep response of neat PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes synthesized at different temperatures for strain amplitudes of $\gamma_0$=0.1-1000% at an angular frequency of $\omega = 10$rad/s using cone-plate geometry (at a truncation of 47µm and cone tip angle of 1°) at 240°C. For sake of easier comparison, storage modulus $G'$ (open black symbols) and loss modulus $G''$ (solid red symbols) values were normalized with respect to their maximum values (Table S1 of Supporting Information, Appendix A). Data points indicated by arrows were used in Figure 3-9 to obtain the Lissajous-Bowditch loops. The insets show magnified $G'$ response of CNT 750/PVDF and magnified $G''$ response of CNT 850/PVDF and CNT 550/PVDF for strain amplitudes of 0.1-10%. As shown by vertical dotted lines, four distinct regimes in the viscoelastic response of poorly-dispersed samples are identifiable as the strain amplitude increases. The first regime (i) corresponds to the linear viscoelastic region (LVR). In the second regime (ii) $G'$ decreased into an intermediate plateau (third regime (iii)), and in the last regime (iv) there is a dramatic decrease in $G'$. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society.

The single-step yielding process in the viscoelastic response of CNT$_{650}$/PVDF by increasing the imposed strain amplitude shows a transition from a solid-like state into a liquid-like state; this could be explained via break-up of hybrid flocculated structures formed by
carbon nanotubes and polymer matrix temporary entanglement network.\textsuperscript{50} In this context, the significant drop in the value of $G'$ can be attributed to the rupture of the filler network; i.e., an irreversible decrease in the number density of elastically active network bonds.\textsuperscript{51}

The multi-step yielding process in poorly-dispersed systems reveals fundamental differences in the microstructure of these samples. This multi-step yielding process can be explained by the subtle movement of aggregates by inter-aggregate bonds rupture under confinement in regime (ii) followed by the break-up of aggregated structures at larger strain amplitudes, i.e., regime (iv). Moreover, densification of particle-rich domains induced by the expulsion of interstitial fluid trapped within the aggregated structures are thought to be responsible for the dissipative process observed during the first yielding process in colloidal systems.\textsuperscript{52} The first drop in storage modulus of CNT\textsubscript{750}/PVDF (see the inset in Figure 3-7) is considerably weaker than CNT\textsubscript{550}/PVDF, CNT\textsubscript{850}/PVDF, and CNT\textsubscript{950}/PVDF, which verifies the better dispersion state in CNT\textsubscript{750}/PVDF. Thus, this behavior is interpreted as the coexistence of well-dispersed and poorly-dispersed carbon nanotube domains in this sample, which is consistent with large agglomeration area and low transparency for CNT\textsubscript{750}/PVDF.

In addition to microstructural changes under intermediate/large strain amplitudes described above, shear flow inhomogeneities might have some impacts on the flow kinematics and the observed viscoelastic response.\textsuperscript{53} Hence, we checked the strain amplitude dependency of the single-step yielding process and multi-step yielding process at different frequencies, CNTs concentrations, and gap-sizes to investigate whether any possible errors arose from flow non-idealities such as slippage at the polymer-plates interfaces (see Figures 3-8, S5, and S6 and the corresponding discussions in Appendix A). These results verify that no wall-slip effect occurred in our rheological observations for neat PVDF and CPNs, even at large deformations. Moreover, the single-step yielding process and multi-step yielding process are frequency-invariant, and the multi-step yielding of poorly-dispersed CNT systems is still observable at an
extremely low frequency of 0.1 rad/s. An extensive discussion can be found in the Supporting Information, Appendix A. However, noticeably multi-step yielding behavior of poorly-dispersed systems showed a strong gap-size dependence due to the confinement of CNTs agglomerates as discussed in the next section.

3.4.5 Gap-size dependence of multi-step yielding.

To demonstrate the effect of confinement on the viscoelastic behavior of the nanocomposites in different regimes defined in Figure 3-7, we performed strain sweep tests for neat PVDF and CNT/PVDF nanocomposites at various gap-sizes. We performed the test for PVDF using cone-plate geometry (cone tip angle of 1° and a truncation of 47 μm) and parallel-plate geometry at a gap-size up to 1000 μm. As can be seen in Figure 3-8, results at different gap-sizes superimpose on each other for neat PVDF, even well into a deeply nonlinear region (regime (iv)), confirming that there is no wall-slip effect. Since our CPNs were pre-compression molded at a thickness of 500 μm, the largest gap-size tested for the CPNs is 400 μm. Similar to neat PVDF, well-dispersed systems (CNT$_{650}$/PVDF and CNT$_{750}$/PVDF) showed no gap-size dependence.

However, as expected from small-amplitude tests (Figure S3 of Appendix A), when the gap-size was increased, viscoelastic functions (e.g., storage modulus) measured for poorly-dispersed systems decreased within the regimes (i) and (ii). The two-step yielding persisted up to a gap-size of 100 μm and disappeared at a gap-size of 400 μm, and the viscoelastic response approached that of the neat PVDF. This data verifies that the gap dependency in our results and the multi-step yielding behavior mainly originate from the confinement of poorly-dispersed CNT structures present in CNT$_{550}$/PVDF, CNT$_{850}$/PVDF, and CNT$_{950}$/PVDF nanocomposite, and not from the slip at metal/sample interface.

This can be better understood if one considers the trends reported for wall-slip effects in suspensions in the literature. For example, we can refer to a work by Barnes.$^{54}$ The author
investigated the typical impact of wall-slip effects on the measured rheological functions at different gap-sizes for yield-stress systems and claimed that as the measuring geometry gap-size increases, a larger value is measured for the rheological functions approaching the no-slip conditions. Based on our observation for poorly-dispersed nanocomposites, an opposite trend is observed, i.e., measured $G'$ in low and intermediate strain amplitudes (regimes (i) and (ii)) decreased as the gap-size increased and at higher amplitudes, regime (iv), all curves superimposed on each other, as shown in Figure 3-8.

Based on the above discussion, one can conclude that poorly-dispersed and isolated CNT domains in the nanocomposite undergo a strong confinement effect at smaller gap-sizes. Hence, in the poorly-dispersed system, the breakage of weak inter-aggregate links under confinement of rheometer plates plays a major role in the first step of the yielding process.

Figure 3-8: Gap-size dependence of storage modulus of neat PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes synthesized at different temperatures using cone-plate geometry (at a truncation of 47μm and cone tip angle of 1°) and parallel-plate geometry at gap-sizes of 100μm, 400μm, and 1000μm at 240°C. Figure S16 of Appendix A shows the loss modulus at different gap-sizes. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society.

Based on all above observations, the first step in structural failure in CNT$_{550}$/PVDF, CNT$_{750}$/PVDF, CNT$_{850}$/PVDF, and CNT$_{950}$/PVDF nanocomposites can be attributed to initial rupture of aggregate-aggregate bonds formed under confinement in the truncation region at
intermediate strain amplitudes, regime (ii). The second step-like feature of the response in regime (iv) can be considered due to extensive structural break-up and disintegration of aggregates and disentanglement of the polymer matrix.\(^5\)

In the next sections, the material response under the LAOS flow and its link to physical/structural features are presented. As previously discussed, LAOS offers a methodology for characterizing nonlinear viscoelastic material functions over a broad domain of amplitudes \((\gamma_0)\) and timescales \((1/\omega)\) of the imposed shear deformation in the capability of a rotational rheometer. So far, we have purely presented lumped viscoelastic functions providing an overall measure of inter-cycle nonlinearity.

It is well known that as the transition into a nonlinear regime takes place, the nonlinear stress response is no longer a single-harmonic sinusoid (see Figure S7 of Appendix A). Analyzing this periodic flow response can provide us with unique insights of nonlinear response, which is not accessible via nonlinear response measures, such as drop in \(G', G''\), etc. In the next sections, we will present a more expansive view of the nonlinear response, as well as intra-cycle nonlinearity parameters.

### 3.4.6 Lissajous-Bowditch plots (intra-cycle viscoelastic behavior).

Figure 3-9 displays the Lissajous-Bowditch loops projections on the elastic \((\tau - \gamma)\) and viscous \((\tau - \frac{dy}{dt})\) planes for data points highlighted in Figure 3-7 at the strain amplitudes of \(\gamma_0 = 1, 4, 39,\) and 620\% (four different regimes) and an angular frequency of \(\omega = 10\) rad/s. For easier comparison, stress, strain, and strain rate values have been normalized with respect to their respective maximum values. In the linear viscoelastic framework, in the elastic projection of Lissajous plots, perfect elastic materials show a straight line (the strain and the stress signals superimpose) and pure viscous materials show a circular shape. Hence, based on the Lissajous concept, viscoelastic materials response will be ellipsoidal in the linear region (see Figure S7 of Supporting Information, Appendix A).\(^5\) Currently, there is no consensus amongst
rheologists on the relationship of the Lissajous loop shapes and the microstructure of the samples. Thus, our aim is to connect the Lissajous plot shapes to the microstructure of our complex fluids.
Figure 3-9: Dimensionless Lissajous-Bowditch loops for PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes synthesized at different temperatures using cone-plate geometry (with a truncation of 47μm and a cone tip angle of 1°) at 240°C. Projections on the elastic ($\tau$ - $\gamma$) and viscous ($\tau$ - $\frac{d\gamma}{dt}$) planes are presented at strain amplitudes of $\gamma_0 = 1, 4, 39, and 620\%$ and an angular frequency of $\omega = 10\text{rad/s}$. In the uppermost left plot, the star symbol shows the strain for flow reversal and the circle symbol shows the maximum stress point. Triangle symbol shows the location of starting the second half-cycle of oscillation. Figure S8 of Appendix A shows the 3-dimensional Lissajous Loops. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society.

As can be seen in the elastic projections, the waveform is a simple ellipse in low strain region ($\gamma_0<40\%$) for neat PVDF and nanocomposites with a good state of dispersion, i.e., CNT$_{650}$/PVDF and CNT$_{750}$/PVDF. As mentioned before, this is a typical response of viscoelastic materials in the linear framework. Increasing the strain leads to an asymmetry of
ellipsoidal shapes and a non-elliptical shape results due to the excitation of higher harmonics. The visual inspection of distortion in Lissajous loops is a good evidence for nonlinearity in materials viscoelastic response.\textsuperscript{57}

In the elastic Lissajous pattern of systems containing CNT\textsubscript{850} and CNT\textsubscript{950}, a nonlinear viscoelastic response is noticeable even at low strains, i.e., strain amplitude of 4\% in regime (ii). The same behavior is seen in the viscous projection Lissajous pattern of CNT\textsubscript{850}/PVDF and CNT\textsubscript{950}/PVDF, and the transition from an ellipsoidal pattern to a complex nonlinear shape is clearly seen even at strain amplitudes as low as 4\%, where the initial departure of linearity appeared in regime (ii) in Figure 3-7. The observed deviation of elastic and viscous Lissajous plots from the ellipsoidal pattern in poorly-dispersed systems at low strain amplitudes in regime (ii) marks a unique response.

The behavior in the elastic Lissajous pattern of systems containing CNT\textsubscript{850} and CNT\textsubscript{950} is in agreement with the data provided in Figures 3-6, S3, and 8. Based on these figures, one can expect a strong solid-like behavior in both regimes (i) and (ii) arising from confinement effect of large agglomerates of CNTs in poorly-dispersed systems in small gap-sizes. As previously mentioned, the trajectory of Lissajous loop in linear framework is elliptical for a viscoelastic material, approaching the limiting case of a straight line for a Hookean elastic solid. Hence, the Lissajous loops tend to be narrow in regime (i) for poorly-dispersed systems due to the quasi-solid bridge formed by big agglomerates of poorly-dispersed systems under confinement of rheometer plats. These structures are collapsed in regime (ii). As the strain amplitude was further increased, the Lissajous pattern approaches that of PVDF in LAOS region in regime (iv). These results are in line with the results of Figure 3-8 where all the data superimposed in LAOS region. Figure S9 of Appendix A shows the gap-size dependency of Lissajous-Bowditch loops of the neat PVDF, the well-dispersed CNT\textsubscript{650}/PVDF system, and the poorly-dispersed CNT\textsubscript{950}/PVDF system.

65
At higher strain amplitude, i.e., regime (iii) and (iv), the stress response became significantly non-sinusoidal and the typical viscous Lissajous loops appeared distorted, indicative of thixotropy and a yielding process in nanocomposite samples. At very large strain amplitudes, i.e., \( \gamma_0 = 620\% \), the viscous Lissajous curves demonstrated a non-elliptical shape with self-intersection (secondary loops), characterizing a strongly nonlinear response. Several authors have interpreted the emergence of secondary loops to be indicative of microstructural changes in the colloidal dispersions under a large amplitude oscillatory shear field. The self-intersection in the viscous projections was accompanied by a strong elastic nonlinearity in the same quadrant of the deformation cycle in the elastic projection curves. The flow direction was reversed at the location of the star symbol in Figure 3-9 (top left Figure) changing to clockwise direction from star symbol to the circle symbol. The stress signal started to increase with the accumulated strain until it reached a maximum value at the location of the circle symbol. The stress then decreased until starting the second half-cycle of oscillation, which was at the location of the triangle symbol (see also Figure S7 (b) for the representation of the shear stress in one cycle of oscillation at strain amplitude of 620\%). This signifies the existence of a local maximum in the elastic projection in regime (iv). After this local peak in the elastic projection, the system starts to flow and the stress decreases. This is similar to the stress overshoot response during the start-up of the steady shear flow. Stress overshoots in LAOS flow would only be expected if the thixotropic restructuring timescale is smaller than the oscillatory deformation timescale. Figure S10 of Appendix A shows that the self-intersection of the viscous Lissajous-Bowditch loops is still observable at the low frequency of 1\,rad/s.

3.4.7 Intra-cycle nonlinear viscoelastic parameters.

The direct consequence of observing a local maximum in the elastic projection is a negative local slope at \( \gamma=0 \), referred to the minimum-strain elastic modulus \( \left. \frac{d\tau}{dy} \right|_{\gamma=0} \equiv G'_M < 0 \).
Similarly, the large-strain elastic modulus is the secant elastic modulus at $\gamma=\pm \gamma_0$, defined as

$$\left. \frac{\tau}{\gamma} \right|_{\gamma=\pm \gamma_0} \equiv G'_L. \quad^{56}$$

In the limit of small strain amplitudes, these parameters converge to the linear elastic modulus $G'$, i.e., $G'_L=G'_M=G'$. These elastic measures have been used by Ewoldt et al.\textsuperscript{56} to develop a dimensionless index for intra-cycle elastic nonlinearity defined as $S \equiv \frac{G'_L-G'_M}{G'_L}$ (strain-stiffening ratio). $S$ value equal to 0 corresponds to a linear viscoelastic response, a positive $S$ indicates intra-cycle strain-stiffening, and a negative $S$ is indicative of intra-cycle strain-softening.

Similar to the above-mentioned elastic measures, viscous parameters have been introduced to characterize intra-cycle viscous nonlinearity. In this context, a set of dynamic viscosities have been defined as the minimum-rate dynamic viscosity $\eta'_M$ and large-rate dynamic viscosity $\eta'_L$.\textsuperscript{56} Similar to the elastic measures, in the linear regime, dynamic viscosities converge to the linear real viscosity value $\eta' = \frac{G'}{\omega}$, i.e., $\eta'_L=\eta'_M=\eta'$. The dimensionless index for dissipative (viscous) intra-cycle nonlinearity has been proposed as $T \equiv \frac{\eta'_L-\eta'_M}{\eta'_L}$ (shear-thickening ratio).\textsuperscript{56} $T=0$ signifies linearity, $T>0$ implies intra-cycle shear-thickening, and $T<0$ corresponds to intra-cycle shear-thinning.

Figure 3-10 depicts the intra-cycle nonlinearity indices for neat PVDF and CNT/PVDF nanocomposites. Using these nonlinear parameters, one can determine the origin of intra-cycle nonlinearity in each regime. In the small strain amplitude limit, i.e., regime (i), both indices, $S$ and $T$, are close to zero and no intra-cycle nonlinearity was detectable. At intermediate strain amplitudes in regime (ii), for CNT\textsubscript{550}/PVDF, CNT\textsubscript{850}/PVDF and CNT\textsubscript{950}/PVDF nanocomposites, the viscous index, $T$, started to increase and reached a maximum, indicating an intra-cycle shear-thickening behavior. However, no measurable elastic intra-cycle
nonlinearity was detected in this regime ($S=0$). This agrees with the results for CNT$_{550}$/PVDF, CNT$_{850}$/PVDF and CNT$_{950}$/PVDF nanocomposites in Figure 3-7, demonstrating a local peak in $G''$ as strain amplitude increases. Thus, this initial intra-cycle shear-thickening viscoelastic behavior coincides with an increase of loss modulus in regime (ii). This indicates that nonlinearity in the intermediate strain range has a purely dissipative origin. The same conclusion can be made based on the area of the elastic non-normalized Lissajous curves in one cycle, which shows the amount of dissipated energy per unit volume at each corresponding strain (see Figure S12 and the corresponding interpretation in Supporting Information, Appendix A). Figure S15 of Supporting Information (Appendix A) verifies that the intra-cycle shear-thickening behavior of poorly-dispersed systems in regimes (ii) and (iii) originates from gap-spanning, jammed structure of the big agglomerates of CNTs formed under confinement of rheometer plates.

At larger strain amplitudes in regime (iii), the $T$ index decreased to values close to zero. Finally, in regime (iv), both indices demonstrated very large positive values, revealing a nonlinear intra-cycle strain-stiffening and shear-thickening behavior. The intra-cycle strain-stiffening behavior in regime (iv) can be correlated to shear-induced stretching and deformation of polymer chains in the nanocomposite samples. The intra-cycle shear-thickening behavior in regime (iv) observed for both the nanocomposites and the neat PVDF, confirmed that this nonlinear viscoelastic character stems from the nature of the PVDF matrix. This result should not be misinterpreted as an increase in viscosity from one cycle of oscillation to another. This could be envisioned as a more rapid decrease in minimum-rate dynamic viscosity ($\eta'_M$) in comparison to large-rate dynamic viscosity ($\eta'_L$) as the strain amplitude increases (see Figure S13 of Appendix A). For further investigation of viscous nonlinear behavior (shear-thickening at extremely large deformations), $T$ index has been measured at two other frequency levels ($\omega=1$rad/s and $\omega=5$rad/s) for neat PVDF. Results of these experiments and related discussions
based on the relaxation process are included in the Supporting Information, Appendix A (see Figure S14).

Figure 3-10: Elastic ($S$) and viscous ($T$) intra-cycle nonlinearity indices as a function of imposed strain amplitude for PVDF and CNT/PVDF nanocomposites containing 1.0wt% of carbon nanotubes synthesized at different temperatures. See Figure S11 of Appendix A for similar results for nanocomposites containing 2.7wt%. Figure S15 of Appendix A shows the gap-size dependency of elastic ($S$) and viscous ($T$) intra-cycle nonlinearity indices for the poorly-dispersed CNT950/PVDF nanocomposite. Reprinted with permission from (Kamkar, Milad, et al. Macromolecules 52.4 (2019): 1489-1504.). Copyright (2019) American Chemical Society.

3.5 Conclusions

In this paper, a series of nanocomposites containing CVD-grown CNTs synthesized at various temperatures, ranging from 550°C to 950°C, were subjected to oscillatory shear deformation in both linear and nonlinear framework. This helped investigate the effects of CNT structure on
Conductive network formation in CNT-based polymer nanocomposites. Utilizing a broad spectrum of characterization techniques, we determined that the synthesis temperature had a great impact on the structure of CNTs (i.e., length, diameter, carbon purity, etc.). Imaging and AC conductivity analyses of the nanocomposites revealed that CNT$_{650}$, due to its high structural purity and geometrical features, had the most well-established conductive network.

The systems had very different rheological properties in both linear and nonlinear regions. The observed intensified solid-like behavior of CNT$_{550}$, CNT$_{850}$, and CNT$_{950}$ at a concentration of 1.0 wt% was attributed to the gap-spanning, jammed structure of the big agglomerates of CNTs or non-CNT constituents clusters, experiencing confinement between rheometer plates. Conversely, CNT$_{650}$ was homogeneously dispersed in the polymer matrix under the applied melting conditions. This has led to more stable CNT network structures under an oscillatory shear-field with an increasing deformation intensity.

The nonlinear rheological behavior of the nanocomposites was studied under LAOS flow to gain further insight into the CNT network structure. All the CNT/nanocomposites, except CNT$_{650}$, exhibited multi-step yielding behavior when the strain amplitude exceeded the linear regime limit. The multi-step yielding behavior was accompanied by a positive shear-thickening ratio, a zero strain-stiffening ratio, and a local peak in loss modulus in intermediate strains. This confirmed the purely dissipative origin of nonlinearity in these systems in the intermediate strain range. We believe that this yielding is due to the densification of particle-rich domains and disruption of big agglomerates of the poorly-dispersed CNTs under rheometer plates confinement.

Results of this work confirmed that the CNTs synthesized at the temperature of 650°C via a chemical vapor deposition (CVD) process possessed a superior nanoscale dispersion state compared to CNTs prepared at the other synthesis temperatures. It was also demonstrated that nonlinear viscoelastic measures are extensively sensitive to subtle changes in internal
microstructures and yield valuable information regarding the nanofiller network structure. This is not necessarily accessible via rheological parameters obtained within the linear framework.

3.6 References


Shields, J. R.; Douglas, J. F. Effects of aspect ratio of MWNT on the flammability properties
of polymer nanocomposites. Polymer 2007, 48 (20), 6086-6096.

on crystalline phases and dielectric properties of poly (vinylidene fluoride). European Polymer


11. Lertwimolnun, W.; Vergnes, B. Influence of compatibilizer and processing conditions on
the dispersion of nanoclay in a polypropylene matrix. Polymer 2005, 46 (10), 3462-3471.


13. Sahebi Jouibari, I.; Kamkar, M.; Nazokdast, H. Nanoparticle effects of thermoplastic
polyurethane on kinetics of microphase separation, with or without preshear. Polymer
Composites.


Ewoldt, R. H.; McKinley, G. H. A review of nonlinear oscillatory shear tests: Analysis and
application of large amplitude oscillatory shear (LAOS). Progress in Polymer Science 2011,
36 (12), 1697-1753.

(vinylidene fluoride) composites. Industrial & Engineering Chemistry Research 2012, 51 (19),
6705-6713.


Chapter 4 - Application of Nonlinear Rheology to Assess the Effect of Secondary Nanofiller on Network Structure of Hybrid Polymer Nanocomposites**

Presentation of the Article:

This Article shows that incorporation of nanowires into CNT-based polymer nanocomposites as secondary nanofillers improves the network structure and dispersion state of nanotubes. The information obtained from rotational rheometry demonstrated that nanowires failed to form an interconnected 3D network in the bulk of the polymer matrix. Hence, the improvement in rheological properties CNT-based polymer nanocomposites upon addition of the nanowires can be solely attributed to enhancement of CNTs’ network structures. These results were confirmed using imaging techniques. Nonlinear rheology was also assisted to get further insights into the network structure of the hybrid nanocomposites. A more severe inter- and intra-cycle nonlinearity was observed by improving CNTs’ network structure by addition of secondary nanofillers. It is worth mentioning that the editors of journal of Physics of Fluids felt that the results of this work are noteworthy, and they promoted this article as “Editors Pick” paper on the website of this journal.

Authors’ contributions: I wrote and organized the paper and performed rheological tests. Dr. Aliabadian helped with rheological interpretation and plotted the graphs. Dr. Zeraati helped with synthesizing and characterizing nanowires and Prof. Sundararaj supervised the whole study.

4.1 Abstract

Carbon nanotube (CNT)/polymer nanocomposites exhibit excellent electrical properties by forming a percolated network. Adding secondary filler can significantly affect the CNTs network, resulting in changing the electrical properties. In this work, we investigated the effect of adding manganese dioxide nanowires (MnO$_2$NW) as a secondary nanofiller on the CNTs network structure inside a poly(vinylidene fluoride) (PVDF) matrix. Incorporating MnO$_2$NW to PVDF/CNT samples produced a better state of dispersion of CNTs, as corroborated by light microscopy and transmission electron microscopy. The steady shear and oscillatory shear flows were employed to obtain a better insight into the nanofiller structure and viscoelastic behavior of the nanocomposites. The transient response under steady shear flow revealed that the stress overshoot of hybrid nanocomposites (two-fillers), PVDF/CNT/MnO$_2$NW, increased dramatically in comparison to binary nanocomposites (single-filler), PVDF/CNT and PVDF/MnO$_2$NW. This can be attributed to microstructural changes. Large amplitude oscillatory shear (LAOS) characterization was also performed to further investigate the effect of the secondary nanofiller on the nonlinear viscoelastic behavior of the samples. The nonlinear rheological observations were explained using quantitative nonlinear parameters (strain-stiffening ratio ($S$) and shear-thickening ratio ($T$)) and Lissajous-Bowditch plots. Results indicated that a more rigid nanofiller network was formed for the hybrid nanocomposites due to the better dispersion state of CNTs and this led to a more nonlinear viscoelastic behavior.
4.2 Introduction

Mixing polymers with carbon nanotubes (CNTs) has attracted considerable attention due to their outstanding properties and related fascinating applications.\textsuperscript{1-4} It is well established that CNT state of dispersion in a polymer matrix has a significant effect on the final properties of the polymer nanocomposites (PNCs).\textsuperscript{3,5} Different strategies have been used to improve the CNT dispersion in a polymeric matrix. For example, functionalization of CNTs by depositing or grafting polymers or functional groups on the external surface of nanofillers (i.e., core-shell structure) is a common strategy to achieve a better CNT dispersion state.\textsuperscript{6,7} Park and Bandaru\textsuperscript{7} showed that functionalization of CNTs with carboxylic groups improved the dispersion state of CNTs and better mechanical properties were achieved using functionalized CNTs. However, CNTs surface modification can be detrimental to CNT intrinsic properties, such as decrease of electrical conductivity and mechanical strength.\textsuperscript{8,9}

Hybrid structures formed by combining secondary fillers with CNT is a promising approach to obtain a better CNT dispersion.\textsuperscript{1,2,10} For instance, Liu et al.\textsuperscript{10} have shown that adding clay as a secondary filler into an epoxy matrix improved the dispersion and distribution of CNTs. The addition of secondary filler can increase the viscosity of the polymer matrix and forces CNT agglomerates to break up and makes it more difficult for nanotubes to re-aggregate.\textsuperscript{10} Another example of the advantage of using a secondary nanofiller to improve CNT dispersion is given by Dang et al.\textsuperscript{2} where adding BaTiO\textsubscript{3} nanoparticles improved the dispersion state of CNT, and also enhanced the dielectric properties of the hybrid nanocomposites. Similar results were obtained by Hayashida and Matsuoka.\textsuperscript{11} Thus, the assessment of the effect of a secondary filler on the CNT state of dispersion is an important factor to understand the final properties of the nanocomposites.

Imaging techniques are commonly used to characterize the state of dispersion of a nanofiller in a polymeric matrix. One of the most widely used methods is electron microscopy.
e.g., Transmission Electron Microscopy (TEM). However, it should be borne in mind that imaging techniques can only provide information about a small part of the sample in the selected field of view, which may not represent the overall nanofiller state of dispersion in the bulk of the system.\textsuperscript{12,13} In addition, these techniques have other disadvantages such as deterioration of the sample when exposed to beams or probes during measurement, or difficulties in sample visualization and focus due to the beam sample depth sensitivity. Furthermore, sample preparation for those techniques may also alter the CNT state of dispersion.\textsuperscript{12}

Rheometry is a powerful tool to characterize the dispersion state and microstructure of nanofillers in the bulk of a polymer matrix because of the large size of sample tested relative to imaging techniques.\textsuperscript{14-16} That is, the macroscopic dimensions of samples give more reliable results compared to techniques where micron size samples are used. Via rheometry, the samples can be tested at different flow conditions. Thus, rheometry provides better understanding of the behavior of the nanocomposite samples during compounding and processing.\textsuperscript{15} Additionally, rheological properties (e.g., storage modulus, loss modulus) are sensitive to any change in the polymer nanocomposites microstructure.\textsuperscript{17} For instance, evaluation of the effect of filler content on the behavior of the elastic modulus at low frequencies under small strain amplitude by applying scaling models makes it possible to correlate them to fractal aggregation of the nanofillers.\textsuperscript{18,19}

The rheological behavior of the nanocomposites can be studied in two regimes: linear and nonlinear viscoelastic regimes. Linear viscoelastic behavior is mostly characterized by small amplitude oscillatory shear (SAOS) flow. Non-terminal behavior,\textsuperscript{20} which suggests a solid-like behavior, is the most widely reported inherent characteristic of polymer nanocomposites under SAOS flow. The increment in the shear viscosity and solid-like behavior in linear framework at high concentrations of the nanofillers are due to the strong entropic and
enthalpic energy barriers due to the strong inter-particle interactions, which leads to frozen or very slowly relaxing structures.\textsuperscript{19,21} On the other hand, strong shear-thinning and amplitude-dependent viscoelastic moduli are the usual rheological behavior of PNCs in nonlinear region under large deformations, e.g., under large amplitude oscillatory shear (LAOS) flow.\textsuperscript{19,22}

The benefit of LAOS over SAOS tests is that LAOS can differentiate complex fluids, which show the same linear viscoelastic behavior under SAOS flow. Moreover, in most industrial processing operations deformations are large, rapid, and non-unidirectional. Thus, from a processing and application point of view, it is important to investigate the rheological behavior of PNCs in the nonlinear framework and correlate their viscoelastic characteristics to the microstructure of the PNCs.\textsuperscript{23} For instance, Hyun et al.\textsuperscript{24} have shown that nonlinear viscoelastic behavior under LAOS flow is sensitive to the polymer composite topology and can help with assessment of dispersion quality or internal structure. Hence, LAOS method delivers a vigorous framework enabling us to map out a rich phenomenology of intracycle nonlinearities, playing an important role in the structure–property relationship of the filler-polymer systems, and thus engineering design.

In the present work, manganese dioxide nanowire (MnO$_2$NW) was used as the secondary filler to improve the dispersion state of CNT. MnO$_2$ is known for its high theoretical specific capacitance, low cost, natural abundance, and environmentally friendly nature.\textsuperscript{25} In our previous study,\textsuperscript{1} we showed that by employing secondary filler, MnO$_2$NW, with similar dimensionality of primary filler, CNT, higher dielectric constant was obtained. To evaluate the microstructure of the nanofillers, the nonlinear rheological properties of CNT/MnO$_2$NW polymer nanocomposites under LAOS and steady shear flow were studied in this work. This approach provides an exceptional opportunity to scrutinize CNTs network structure via investigating the viscoelastic parameters. The nonlinear oscillatory rheological results were mainly presented using qualitative closed loops of shear stress vs. strain and shear stress vs.
strain rate (“Lissajous-Bowditch” curves which we will simplify as “Lissajous”) and physical interpretation based on mathematical criteria related to nonlinear viscoelastic parameters. We used transmission electron microscopy and optical microscopy to verify the rheological observations. The dielectric analysis of the samples used in the current study, which revealed better state of dispersion for CNTs in the presence of secondary nanofiller, can be found in our previous work.¹

4.3 Experiments and material characterizations

4.3.1 Nanocomposites preparation

MnO₂ nanowires used in this study were synthesized by a hydrothermal method. Details on the synthesis of MnO₂ nanowires can be found elsewhere.²⁵ PVDF (3M Canada, PVDF 11008/0001), selected as the polymer matrix, and multi-wall carbon nanotubes (CNTs), Nanocyl™ NC7000, as the primary nanofiller, were used without further treatment. Binary, PVDF/CNT and PVDF/MnO₂NW, and also hybrid nanocomposites (two-filler), PVDF/CNT/MnO₂NW, were fabricated by melt mixing and using APAM (Alberta Polymer Asymmetric Minimizer) at 240°C and 235rpm. Binary nanocomposites of PVDF/CNT and PDVF/MnO₂NW with different concentration were prepared with 15min mixing after 3min PVDF mastication. PVDF/CNT/MnO₂NW hybrid nanocomposites, at each CNT concentration (0.5, 1.0, 1.5 and 2.0wt%), with different MnO₂NW/CNT weight ratios (1 and 2) were fabricated. To do this, PVDF was masticated for 3min, followed by the addition of CNTs and mixing for 7min. Finally, MnO₂NW were added and mixed for an additional 8min for CNT/MnO₂NW hybrid nanocomposites. A Carver compression molder (Carver Inc., Wabash, IN) was used to make disc-shaped samples at 240°C and 35MPa for 10min. The diameter and thickness of the samples were 25mm and 0.2mm respectively.
4.3.2 Transmission electron microscopy

The structure of polymer nanocomposites was studied by high-resolution transmission electron microscopy (HRTEM). The TEM micrographs of MnO$_2$NW and polymer nanocomposites were taken using Tecnai TF20 G2 FEG-TEM (FEI, Hillsboro, OR) at 200kV acceleration voltage. The images were captured by a Gatan UltraScan 4000 CCD Camera (Gatan, Pleasanton, CA). For the TEM analysis of the nanocomposites, the nanocomposites samples were cryo-ultramicrotomed to provide sections of ~70nm in thickness using a Cryo Leica EM UC7.

4.3.3 Light transmission microscopy

The state of the microdispersion of nanofillers within the PVDF matrix was analyzed using light transmission microscopy (LM) on thin cuts (2μm thickness) of the compression molded samples, prepared with a Leica microtome RM2265 (Leica Microsystems GmbH, Wetzlar, Germany) equipped with a diamond knife at room temperature. An Olympus® BX60 optical microscope (Olympus Inc, USA) connected to an Olympus DP80 camera was used to capture images with dimensions of 600 × 800μm$^2$ from different cut sections.

4.3.4 Rheology

Rheological measurements were performed under a nitrogen atmosphere to reduce degradation of polymer chains using an Anton-Paar MCR 302 rheometer equipped with 25mm diameter parallel plates with a gap size of 0.2mm. All experiments were carried out using stress-controlled mode at 240°C. To reach the desired condition (stable temperature and nanocomposite morphology), a rest time of 10min in the rheometer was used after loading the sample. Time sweep SAOS measurements were performed on the samples at 240°C confirming that no degradation of the samples occurred after the long-time exposure at elevated temperatures. Strain amplitude sweep experiment was carried out on all samples to determine the linear viscoelastic regime (LVR). This test was done over a range of applied strain...
amplitudes from 0.1 to 1000% at an angular frequency of 1 rad/s. Based on the results of this experiment, the strain amplitude of 0.1% was determined to be small enough to keep the deformation in the linear viscoelastic regime. The linear viscoelastic regime is very sensitive to structure evolution. Thus, in this study, the results of time sweep test after start-up of shear flow were studied at angular frequency of 1 rad/s and strain amplitude of 0.1% to investigate the structural evolution of the samples and determine the extent of network formation. During this test, the storage modulus \( G' \) was monitored. To apply the start-up of steady shear flow test, a constant shear rate of 1.0 s\(^{-1}\) was imposed on the samples.

To get the LAOS results, the rheometer was placed in a rigid and mechanically stable environment to minimize any mechanical noise. To obtain last full waveform of shear stress at each strain amplitude, samples were strained at a constant frequency and amplitude. LAOS data were collected after 5-6 cycle for each strain amplitude.

### 4.4 Results and discussion

#### 4.4.1 Nanofiller characterization

TEM micrographs of MnO\(_2\)NW are shown in Figure 4-1a-b. Image analysis of synthesized nanowires shows that the length and diameter are about 2.0\( \mu \)m and 57 nm, respectively. TEM images reveal the match dimensionality between primary filler, CNT, and secondary filler, MnO\(_2\)NW. The XRD pattern of as-synthesized MnO\(_2\)NWs is shown in Figure 4-1c. The diffraction peaks can be finely assigned to the pure tetragonal \( \alpha \)-MnO\(_2\).\(^{26}\) Furthermore, XRD and TEM results show the high purity of synthesized MnO\(_2\)NW.
In the first stage of rheological characterizations, start-up shear test was used to study nanofiller network structure through the polymer media. The transient shear stress response ($\tau$) starts with a linear increment until time $t_{max}$, and then decreases from the maximum value $\tau_{max}$ toward a steady-state value. The emergence of overshoot is considered as a signature of the network structure rupture. This overshoot was reported by several authors for polymer nanocomposites.\textsuperscript{28-30}
The magnitude of the overshoot is a measure of the network strength and the accumulation of elastic energy in the clusters.\textsuperscript{31} For polymer nanocomposites at melt state, the stress overshoot is attributed to the failure of the nanofiller network and fluidization. It is also due to the orientation of highly anisotropic individual nanofillers in the direction parallel to the shear axis.\textsuperscript{32} Thus, it can be considered to signal the transition from pseudo-solid-like behavior to liquid-like behavior.\textsuperscript{33} The orientation of mesostructured materials such as block copolymers, liquid crystalline materials, nanofillers (in polymer nanocomposites) under sufficiently large deformation is well documented.\textsuperscript{34-36} For a specific polymer matrix filled by nanofillers, the structure of the nanofillers network depends on concentration and dispersion quality of the nanofillers. Therefore, the transient response to nonlinear deformation can be an effective test to investigate the structure of nanofillers in a polymer media.

Figure 4-2: Shear stress as a function of time at $T=240^\circ C$ and $\dot{\gamma} = 1.0s^{-1}$ for neat PVDF and nanocomposites.

Figure 4-2 indicates different levels of overshoot for binary nanocomposites and hybrid nanocomposites. There is no significant stress overshoot for neat PVDF. The small overshoot of PVDF can be related to the molecular weight of PVDF that is over the entanglement molecular weight. Comparing stress overshoots of PVDF/2.0wt%MnO$_2$NW and PVDF/1.0wt%CNT nanocomposites reveals dissimilarity in the nanofiller network structure of
these samples. It is postulated that the concentration of MnO$_2$NW is not high enough to form a stiff 3D network. In fact, the number of fillers in the PVDF/1.0wt%CNT nanocomposite is much higher than the PVDF/2.0wt%MnO$_2$NW nanocomposite (see the TEM images in Figure 4-3). This is due to lower density of CNT (~1.7g/cm$^3$) in comparison to MnO$_2$NW (~5.03g/cm$^3$). Thus, the polymer-nanofiller interface area is higher in PVDF/1.0wt%CNT nanocomposites, and due to reinforcement effect of CNT-polymer through the interface, CNTs form a more rigid network through the bulk of PVDF. As a result, overshoot is much higher for this nanocomposite compared to PVDF/2.0wt%MnO$_2$NW nanocomposite. Moreover, the higher flexibility of CNT$^{37}$ in comparison to MnO$_2$NW is another reason for huge differences in their network structure and mechanical integrity due to elastic interlocking and self-aggregation of CNTs.$^{38,39}$

More importantly, a much higher stress overshoot is observed for hybrid nanocomposites. It is clear that MnO$_2$NWs do not form a stiff network structure and their network is much weaker than the CNTs network, thus MnO$_2$NWs do not have a significant contribution to the network formation. Hence, the sharp increment of stress overshoot in hybrid nanocomposites compared to binary nanocomposites can be accredited to the improvement in dispersion state of CNTs. It should be mentioned that the other prepared nanocomposites showed the same behavior. As an example, the start-up results of nanocomposites containing 2.0wt%CNT with different ratios of MnO$_2$NW are presented in Figure S1 of Appendix B.

To have better insight into the microstructure and dispersion state of nanofillers in polymer nanocomposites, TEM was carried out on the PVDF/1.0wt%CNT, PVDF/1.0wt%CNT/1.0wt%MnO$_2$NW, PVDF/1.0wt%CNT/2.0wt%MnO$_2$NW, and PVDF/2.0wt%MnO$_2$NW samples (see Figure 4-3). For PVDF/1.0wt%CNT nanocomposite, TEM images reveal CNTs form large agglomerates. As can be seen in the TEM images of the hybrid nanocomposites, MnO$_2$NWs improve the dispersion state of CNTs by decreasing the
agglomerates size and increasing the number of individual dispersed CNTs. Light microscopy of the prepared nanocomposites (Figure 4-4) shows the same result. That is by adding MnO₂NW to PVDF/CNT nanocomposites, big agglomerates break into smaller ones and PVDF/1.0wt%CNT/2.0wt%MnO₂NW has a better dispersion state than PVDF/1.0wt%CNT. Moreover, Table 4-1 indicates the agglomerate area decreased for hybrid nanocomposites.

Figure 4-3: TEM images of (a) PVDF/1.0wt%CNT, (b) PVDF/1.0wt%CNT/1.0wt%MnO₂NW, (c) PVDF/1.0wt%CNT/2.0wt%MnO₂NW, and (d) PVDF/2.0wt%MnO₂NW.

Figure 4-4: Light microscopy of (a) PVDF/1.0wt%CNT, (b) PVDF/1.0wt%CNT/1.0wt%MnO₂NW, (c) PVDF/1.0wt%CNT/2.0wt%MnO₂NW, and (d) PVDF/2.0wt%MnO₂NW.
Table 4-1: Agglomerate area for nanocomposites

<table>
<thead>
<tr>
<th>Nanocomposites</th>
<th>Agglomerate area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF/1.0wt%CNT</td>
<td>4.4 ± 0.4</td>
</tr>
<tr>
<td>PVDF/1.0wt%CNT/1.0wt%MnO₂NW</td>
<td>3.6 ± 0.3</td>
</tr>
<tr>
<td>PVDF/1.0wt%CNT/2.0wt%MnO₂NW:</td>
<td>3.8 ± 0.4</td>
</tr>
</tbody>
</table>

Figure 4-5: Schematic of the dispersion state of CNTs and the interaction area between the polymer and nanofillers in (a) PVDF/CNT nanocomposite and (b) PVDF/CNT/MnO₂NW hybrid nanocomposite.

Obviously, the final structure of nanofillers in polymer matrix depends on both the particle-particle interaction and particle-matrix interaction. Improvement in the dispersion state of CNTs leads to more individual CNTs and also smaller agglomerates (see Figure 4-5). Due to these factors, the number of direct bridges and primary entanglements would be increased in hybrid nanocomposites resulting in a stronger mechanical network. Therefore, it can be alleged that adding MnO₂NW leads to an appreciable change in the network structure of CNTs. Thus, the larger stress overshoots observed in start-up experiments for the hybrid nanocomposites at a constant amount of CNTs can be attributed to the effect of the secondary nanofiller on dispersion state of CNTs.
4.4.3 Storage modulus recovery

It is well known that storage modulus ($G'$) is highly sensitive to the structure evolution within the nanocomposites.\textsuperscript{17,41} To investigate the extent of restructuring and elastic recovery, $G'$ was monitored versus time immediately after start-up shear test. According to the recent study by Ranjbar et al.\textsuperscript{42}, the elastic recovery of samples during annealing time is divided into two steps. In the first step, the fast recovery of storage modulus at short times for samples containing nanofillers is attributed to network restructuring. Therefore, the initial intensification of modulus is due to joining of the existing clusters and aggregation of un-oriented nanofillers to form a 3D network structure. The restructuring in this stage is mainly controlled by particle-particle and particle-matrix interactions. In the second stage of restructuring, which is controlled by Brownian diffusion, the state of orientation created during the shearing is lost and a more isotropic state results.

Figure 4-6 illustrates the result of the storage modulus recovery versus annealing time for neat PVDF and nanocomposites. In Figure 4-6, neat PVDF shows a smooth increase in the storage modulus. Moreover, it does not exhibit significant stress overshoot in transient shear stress response in Figure 4-2. According to these results, for samples containing PVDF as the matrix, the molecular relaxation does not have any significant contribution to the storage modulus recovery. For the sample containing 2.0wt\%MnO$_2$NW, the storage modulus does not increase as much compared to the sample with only 1.0wt\%CNT. The other noticeable feature in Figure 4-6 is the dramatic increase of the storage modulus for the hybrid nanocomposites (from about 3kPa for PVDF to 25kPa for PVDF/1.0wt\%CNT/2.0wt\%MnO$_2$NW). The increase of the modulus in this test is not only a function of nanofiller concentration\textsuperscript{43,44} but also a function of the dispersion state of the nanofillers. While the contribution of the MnO$_2$NW alone to modulus recovery is minimal, the sharp increase in the modulus recovery of the hybrid nanocomposites can be attributed to the improvement of the CNTs dispersion state due to the
existence of the secondary filler (MnO₂NW). These results are in line with start-up shear test results.

Figure 4-6: Storage modulus recovery after cessation of flow at $\omega = 1.0\text{rad/s}$ and $\gamma_0 = 0.1\%$ for neat PVDF and nanocomposites.

4.4.4 Effect of secondary nanofiller on LAOS flow and nonlinear viscoelastic parameters

As mentioned before, polymer nanocomposites are in their nonlinear viscoelastic framework during processing. Therefore, to study the viscoelastic behavior in the nonlinear regime, oscillatory strain amplitude sweep test was conducted on the samples. Figure 4-7 shows the results of oscillatory strain amplitude sweep. At low strain amplitude region, samples depict no dependency on the input strain amplitude. The transition from the linear regime to nonlinear regime occurs as the strain amplitude exceeds the critical strain amplitude. This transition takes place at the strain amplitude when the value of $G'$ starts to decrease, which is a typical feature of entangled polymeric materials. This decrease in $G'$ occurs due to the slippage of chain entanglements and motion of the chains with free ends. The value of the critical strain amplitude decreases for PNCs because of the presence of a strain sensitive rigid network structure through the polymer media, which is more likely to break down at lower strain amplitudes. The main underlying mechanism corresponds to this yielding process in PNCs at
the critical point is stochastic erosion, i.e., the breakdown of the filler agglomerates or network\textsuperscript{44,45} and nanofiller-matrix slippage,\textsuperscript{46,47} which leads to a decrease in the density of load-bearing network structures.\textsuperscript{48,49} The mentioned mechanisms depend on the dispersion state and separation of the nanotubes in the polymer matrix.\textsuperscript{50} Thus, the decrease of the critical strain amplitude is more pronounced for hybrid nanofillers, which signifies a fundamental difference in hybrid nanocomposites network compared to the binary PNCs.

![Graph showing strain amplitude sweep measurement at $\omega = 1.0 \text{rad/s}$ on neat PVDF and nanocomposites, arrows show the critical strain amplitude (transition from linear regime to nonlinear regime).](image)

To further investigate the nonlinear properties of polymer nanocomposites under LAOS flow, the nonlinear parameters obtained from data points in Figure 4-7 are presented in this segment. LOAS flow is a function of at least two parameters: strain amplitude deformation and angular frequency. Independently controlled strain amplitude and frequency allows us to access a wide range of nonlinear behavior- this is the greatest advantage of LAOS measurements.\textsuperscript{51,52} Thus, LAOS tests have been widely used as an effective technique to study the nonlinear viscoelasticity due to any change in topology, morphology, and concentration.\textsuperscript{53,54} In the present work, we investigated the nonlinear rheological response of PNCs by increasing the
input oscillatory strain amplitude \( (\gamma = \gamma_0 \sin(\omega t)) \) at a constant angular frequency of 1.0rad/s. Under LAOS flow, the input sinusoidal strain signal is translated to a non-sinusoidal stress signal. Different methods are used to analyze the non-sinusoidal output stress response. Fourier transform rheology (FT-rheology)\(^{55}\) and stress decomposition\(^{56}\) are the most common ones. For example, the shear stress \((\sigma)\) response to an input oscillatory strain at steady-state condition can be written as an in-phase component and an out-phase component and represented as a time-domain Fourier series of odd harmonics\(^{57,58}\):

\[
\sigma(t) = \gamma_0 \sum_{n=1}^{N} \left[ G'_n(\omega, \gamma_0) \sin n\omega t + G''_n(\omega, \gamma_0) \cos n\omega t \right] \quad (4-1)
\]

where \(\gamma_0\) is strain amplitude, \(G'_n\) and \(G''_n\) are amplitudes of the \(n\) harmonics with frequencies \((n\omega)\). For materials in linear viscoelastic region, the output stress signals are a sinusoidal wave, which can be simply characterized by only the first harmonic coefficient, \(n = 1\), with a temporal phase shift \((\delta_1 = G''_1/G'_1)\). The appearance of higher order harmonics indicates nonlinearity in the viscoelastic behavior, meaning that it cannot be described simply by sinusoidal waves. Moreover, in nonlinear regime, the measured moduli \((G'_1\) and \(G''_1\)) do not have a clear physical meaning, which means another method must be applied to interpret the stress signal. Thus, we used the following method to describe the physical meaning of nonlinear parameters.

The shear stress response \((\sigma(t))\) can be decomposed into an elastic stress component \((\sigma')\) and a viscose stress component \((\sigma'')\) as an odd function of normalized strain \((x(t) = \frac{\gamma(t)}{\gamma_0})\) and normalized strain rate \((y(t) = \frac{\dot{\gamma}(t)}{\gamma_0})\), respectively. Thus, the total shear stress can be expressed as:

\[
\sigma(t) = \sigma'(t) + \sigma''(t) \quad (4-2)
\]
A series of Chebyshev polynomials of the first kind\cite{59,60} in the orthogonal space made up of the input strain and strain-rate can be used to represent the elastic and viscous stress components via the following equations:

\[
\sigma'(x; \omega, \gamma_0) = \gamma_0 \sum e_n(\omega, \gamma_0) T_n(x) \quad (4-3)
\]

\[
\sigma''(y; \omega, \gamma_0) = \dot{\gamma}_0 \sum v_n(\omega, \gamma_0) T_n(y) \quad (4-4)
\]

where \(T_n\) is the \(n\)th-order Chebyshev function and “\(e\)” and “\(v\)” are Chebyshev weighting coefficients and are a physical interpretation of the elastic and viscous contributions and have the same units of linear modulus and viscosity, respectively.

The criteria for specification of the physical interpretation of the nonlinearity based on “\(e\)” and “\(v\)” is defining the concavity of \(\sigma'\) and \(\sigma''\). As the magnitude of each Chebyshev coefficient decays monotonically by increasing “\(n\)”, the third-order Chebyshev coefficients \((e_3\) and \(v_3\)) determine the concavity of the elastic and viscous stress curves. According to these coefficients, the following intracycle nonlinear behaviors can be observed: strain-stiffening \((e_3 > 0)\), strain-softening \((e_3 < 0)\), shear-thickening \((v_3 > 0)\) and shear-thinning \((v_3 < 0)\).\cite{53}

Figure S2 and S3 of Appendix B depict the normalized Chebyshev spectrums \((e_3/e_1\) and \(v_3/v_1\)) of our samples.

Similarly, comparison of nonlinear viscoelastic moduli \((G'_M\) and \(G'_L\)) and dynamic viscosities \((\eta'_M\) and \(\eta'_L\)) can give us good insight into the nonlinear behavior. From the mathematical point of view, the large-strain modulus \(\left.\frac{\sigma}{\gamma}\right|_{\gamma=\pm\gamma_0} \equiv G'_L\) is the secant elastic modulus at the point where deformation is maximum \((\gamma = \pm\gamma_0)\), and the minimum-strain modulus \(\left.\frac{d\sigma}{d\gamma}\right|_{\gamma=0} \equiv G'_M\) is the derivative of the stress with respect to strain at the point where deformation takes a zero value \((\gamma = 0)\) (Figure S4 of Appendix B). Both \(G'_M\) and \(G'_L\) converge to linear elastic modulus in the linear viscoelastic region, i.e., \(G'_M = G'_L = G'.\)\cite{59} Likewise,
minimum-strain rate viscosity \( \left( \frac{d\sigma}{dy} \right)_{\gamma=0} \equiv \eta'_M \) is the derivative of the stress with respect to the strain rate at the point where strain rate is minimum and large-strain rate viscosity \( \left( \frac{\sigma}{y} \right)_{\gamma=\pm\gamma_0} \equiv \eta'_L \) is measured at the point where strain rate is maximum (Figure S4 of Appendix B).

Based on the definition of \( G'_M \) and \( G'_L \), strain-stiffening ratio is defined as \( S = \frac{G'_L - G'_M}{G'_L} \) and is zero in the linear viscoelastic region, positive for intracycle strain-stiffening response, and negative for intracycle strain-softening behavior.\(^\text{59}\) In the same way, shear-thickening ratio \( (T = \frac{\eta'_L - \eta'_M}{\eta'_L}) \) can be used to evaluate nonlinear viscous properties of a media during an increase or decrease in the shear rate. Linear viscoelastic behavior occurs when \( T = 0 \), while shear-thinning and shear-thickening behaviors occur when \( T < 0 \) and \( T > 0 \), respectively.\(^\text{59}\)

Figure 4-8 and 4-9 show the \( S \) and \( T \) indices versus input strain amplitude, respectively. In the small strain amplitude region, both indices, \( S \) and \( T \), are close to zero indicating linear viscoelastic behavior. Beyond the linear viscoelastic regime, the positive \( S \) and negative \( T \) for the samples indicate intracycle strain-stiffening and shear-thinning behavior, respectively. According to Figure 4-8, neat PVDF has a higher \( S \) ratio than the PVDF nanocomposites at maximum deformation (strain amplitude of 1000%) due to the high deformation and shear-induced stretching in polymer chains extending into the non-Gaussian regime.\(^\text{61}\) This ratio decreases for the binary PNCs, which means the chains of the polymer are less stretched in the presence of the nanofillers, which is in line with previous finding.\(^\text{62}\) Moreover, \( S \) ratio is smaller for PVDF/1.0wt%CNT nanocomposite in comparison to PVDF/2.0wt%MnO\(_2\)NW nanocomposite, resulting from the reinforcement effect of CNTs (due to the existence of a higher number of nanofillers in PVDF/1.0wt%CNT and strong interactions along a huge interfacial area between the CNTs and polymer matrix). For hybrid nanocomposite, higher
dispersion of CNTs leads to smaller deformation of the individual chains and hence smaller $S$ index and intracycle strain-stiffening behavior.

Based on Figure 4-9, $T$ index decreases for all samples at high strain amplitudes due to intracycle shear-thinning behavior. The viscosity of neat PVDF is almost independent of strain amplitude. Thus, $T$ is roughly zero up to high strain amplitudes for neat PVDF. The nanocomposite containing 1.0wt%CNT exhibits strong intracycle shear-thinning behavior. The strong shear-thinning behavior of PVDF/1.0wt%CNT nanocomposite could be attributed to disruption of local tube contacts and orientation of the nanotubes and rigid molecular chains in the polymer at large deformations with the flow direction. The strain amplitude sensitivity of $T$ index reveals that intracycle shear-thinning behavior occurs more extensively in hybrid structure, and $T$ index diverges more significantly from zero. Moreover, as can be seen in Figure 4-9, $T$ decreases with steeper slope at intermediate strain amplitudes ($40% < \gamma < 200\%$) for the hybrid structure compared to binary nanocomposites and neat PVDF. This is due to higher sensitivity of the rigid hybrid network structure to the input strain, which is more likely to break down at lower strain. After disruption of the hybrid structure, the $T$ index continues the decreasing trend with the same rate of other samples. Thus, the nonlinearity begins sooner with higher intensity for hybrid nanocomposite system. This is consistent with previous research done by Papon and coworkers.63
4.4.5 Lissajous-Bowditch plots

The form of the Lissajous plots can be used for characterization of the material’s viscoelastic behavior at low, intermediate, and high strain amplitudes. Figure S4 of Appendix B presents a schematic of Lissajous patterns plots. In the elastic projection of Lissajous plots, perfect elastic materials show a straight line (i.e., the strain and the shear stress signals superimpose) (Figure S4c of Appendix B) and in the viscous projection of Lissajous plots, pure viscous materials
show a straight line (Figure S4d of Appendix B). Based on the Lissajous concept, viscoelastic materials response in linear regime is ellipsoidal\textsuperscript{59} (Figure S4b). The distortion from the linear viscoelastic pattern (ellipsoidal shape) shows the contribution of the higher harmonics in shear stress waveforms and the extent of nonlinearity.\textsuperscript{58,64} Additionally, Lissajous curves facilitate the qualitative assessment of nonlinear behavior and give us a good idea of nonlinear viscoelastic behavior.\textsuperscript{59} The challenge for rheologist is to correlate the shape of these curves in the nonlinear framework to the microstructure of the samples. In this section, the relation between the shape of the Lissajous curves and the microstructure of our complex fluid is studied.
Figure 4-10: Elastic Lissajous-Bowditch curves (normalized total shear stress $\frac{\sigma}{\sigma_{\text{max}}}$(solid lines) and normalized elastic stress $\frac{\sigma'}{\sigma_{\text{max}}}$ (dotted lines)).
Figure 4-11: Viscous Lissajous-Bowditch curves (normalized total shear stress $\frac{\sigma}{\sigma_{max}}$ (solid lines) and normalized viscous stress $\frac{\sigma''}{\sigma_{max}}$ (dotted lines)).

Figure 4-10 and 4-11 present Lissajous curves in terms of total shear stress $\sigma(t; \gamma, \omega)$ (hysteresis loops) and elastic stress $\sigma'$ (dotted lines) versus the strain amplitude ($\gamma$) and the total shear stress $\sigma(t; \gamma, \omega)$ (hysteresis loops) and viscous stress $\sigma''$ (dotted lines) as a function of shear rate ($\dot{\gamma}$). For easier comparison stress, strain, and strain rate values were normalized with respect to maximum values. As can be seen from Figure 4-10, for neat PVDF, the Lissajous patterns are ellipsoidal in the linear region, i.e., at small strain amplitudes. In addition, elastic stress response (dotted line) at respective strain amplitude is proportional to $\gamma_0$ and the resulting $G'$ is independent of $\gamma_0$. Thus, this system exhibits essentially linear viscoelastic behavior and the contribution of the higher harmonics is zero in the linear framework. As the strain amplitude exceeds the limit of the linearity, deviation from linearity of elastic contribution and asymmetry of ellipsoidal shapes occur due to the existence of the higher harmonics. The slope of the elastic stress contribution deviates from a straight line, which shows the strain dependency of the $G'$ in nonlinear framework. This anomalous behavior
in large amplitude region helps us to distinguish linear and nonlinear viscoelastic regimes. Moreover, Lissajous plots can help with the determination of the nonlinear viscoelastic behavior. In this regard, the concavity of the elastic stress in positive domain ($\gamma > 0$) is upward, which shows that samples have an intracycle strain-stiffening behavior in the nonlinear region (see black dotted lines in Figure 4-10).

Introducing CNTs to polymer matrix changes the shape of the total shear stress loops to an anisotropic ellipsoidal shape in the lower strain amplitude region, which is easily noticed. The major axis of the ellipses rotates counter-clockwise marginally (the non-normalized Lissajous loops in Figure S5 in supporting information, Appendix B, show the rotation with better resolution) and the elastic stress contribution turns to a curvy line at lower strain amplitudes for PNCs in comparison to neat PVDF. This behavior is an indicative of thixotropic behavior and yielding process in PNCs$^{65,66}$ and indicates that the viscoelastic behavior of PNCs even at low strain amplitudes is different from the behavior of the homopolymer. As mentioned, the deviation in linearity of elastic stress becomes more pronounced for PNCs. Similar results were observed by Lim et al.$^{67}$ on PCL/MWNT. They showed nonlinear behavior was more evident for PNCs due to their complicated inner structure and to network rupture, i.e., where the filler network structure goes through a significant breakdown and the nanofillers align to the flow direction. Concentration, size, shape, surface functionality, and the state of dispersion can affect the viscoelastic behavior of the systems.$^{68}$ Thus, the loops show a wide lozenge pattern instead of the elliptical pattern for hybrid nanocomposite at the strain amplitude of 100% (for better comparison see Figure S5 of Appendix II). This is due to better dispersion of CNTs and existence of the secondary nanofiller. By further increasing the strain amplitude, the Lissajous curves show a rectangular pattern and the nonlinear effects become more apparent (the slope of elastic stress changes with increment in strain amplitude). Additionally, the area of the total shear stress loop in one cycle in elastic projection can be used to determine the
dissipated energy per unit volume. Figure S5 of Appendix B shows the non-normalized total shear stress versus strain amplitude at the strain amplitude of 100%. The much bigger area of the total shear stress curve for hybrid nanocomposite indicates higher dissipated energy due to its specific microstructure.

Figure 4-11 shows the viscous projection of Lissajous curves. The viscous stress contribution changes linearly with the shear rate at low deformations, which represents Newtonian behavior. By increasing the strain amplitude, the slope of the viscous stress (dotted lines) becomes strain rate dependent. The downward concavity of the viscous stress at high shear rates illustrates intracycle shear-thinning behavior in samples. The distortions in the nonlinear framework for both elastic and viscous contributions is much more evident for hybrid nanocomposite, which is a direct consequence of microstructure effect of the nanofillers network on viscoelastic behavior.

4.5 Conclusions
Since viscoelastic properties of polymer nanocomposites are extremely sensitive to the microstructure of the nanofillers, rheology provides a powerful tool to evaluate the nanofiller dispersion state through a polymeric matrix. In the current study, the effect of adding secondary nanofiller, MnO$_2$NW, on nonlinear viscoelastic responses of PVDF/CNT polymer nanocomposites was investigated. Start-up shear test was employed to investigate the network structure of the nanofillers through the samples. It was shown that the overshoot of polymer nanocomposite containing 2.0wt%MnO$_2$NW was smaller than polymer nanocomposite containing 1.0wt%CNT. However, adding MnO$_2$NW as a secondary filler to PVDF/1.0wt%CNT dramatically increased the overshoot. Thus, it can be concluded that adding MnO$_2$NW to PVDF/CNT nanocomposites improved the dispersion state of CNTs and this was confirmed by image analysis.
Further investigation of nanofiller superstructures was done by LAOS tests using quantitative (strain-stiffening and shear-thickening indices) and qualitative (Lissajous-Bowditch curves) analysis. The nonlinear rheological response of hybrid nanocomposites (two-fillers; PVDF/CNT/MnO$_2$NW) featured fundamental differences compared to binary nanocomposites (one-filler; PVDF/CNT and PVDF/MnO$_2$NW). The lower strain-stiffening ratio ($S$) for hybrid polymer nanocomposite, due to change in internal structure, shows lower deformation of polymer chains in hybrid polymer nanocomposites compared to that in single filler polymer nanocomposites. Additionally, intracycle shear-thinning behavior occurred more intensively for hybrid structure. The interpretation of the Lissajous curves provided the same conclusions about the internal structure of the polymer nanocomposites in terms of the network structure. The difference in distortion and surface area of the Lissajous loops suggested a completely different network structure in single filler polymer nanocomposites versus hybrid polymer nanocomposites, resulting in large property contrast. These fundamental differences can be attributed to different dispersion state of CNTs in the presence of MnO$_2$NW. Based on these results, the hybrid nanocomposites with better dispersion state had higher number of nanofiller-nanofiller and nanofiller-polymer interaction sites. Consequently, the rigid network of the hybrid nanocomposites was much more sensitive to deformation (i.e., input strain amplitude), which was captured by nonlinear viscoelastic measurements.

### 4.6 References


Chapter 5 - The Key Role of Processing in Tuning Nonlinear Viscoelastic Properties and Microwave Absorption in CNT-based Polymer Nanocomposites

Presentation of the Article:

This paper is oriented to study the nonlinear viscoelastic response of CNT-based polymer nanocomposites prepared by two frequently-used mixing techniques namely, melt and solution mixing. Prior to rheological tests, nanocomposite samples were characterized using imaging techniques and electrical measurements. In this regard, the segregated structure observed in solution-mixed samples showed higher electrical properties. In line with electrical measurements, higher linear viscoelastic properties (e.g., storage modulus) was observed for solution-mixed samples. In the last step of this work, nonlinear viscoelasticity of solution-mixed and meld-mixed samples were compared to elucidate the effect of processing approach on LAOS behavior of the CNT-based nanocomposite samples. Results showed that solution-mixed samples, with a stronger network, exhibited higher nonlinearity as verified by emergence of a self-intersection in viscous projection of Lissajous-Bowditch plots.

Authors’ contributions: I organized the work and wrote the manuscript. I also performed the rheological characterizations. Ms. Sultana help with preparation and characterization of the nanocomposites. Miss. Eshraghian and Miss. Erfanian helped with capturing OM images. Dr. Pawar helped with interpretation of EMI data. Prof. Sundararaj supervised the whole study.

** Materials Today Communications (2020): 101010,

https://doi.org/10.1016/j.mtcomm.2020.101010
5.1 Abstract

Multi-walled carbon nanotube (MWCNT)/polymer nanocomposites exhibit excellent microwave shielding properties by forming interconnected networks of MWCNT in the polymer matrix. However, the final properties of MWCNT-based nanocomposites greatly depend on the quality of MWCNT dispersion, hence on the mixing technique. In the current work, for the first time, we study the effect of different mixing methods on nonlinear viscoelastic response and electromagnetic interference shielding effectiveness (EMI SE) of MWCNT/polymer nanocomposites. To do this, MWCNT/poly(styrene) (PS) nanocomposites were prepared by two frequently-used approaches, namely, melt mixing and solution mixing. Probing the nonlinear rheological response of the samples reveals higher intra-cycle and inter-cycle viscoelastic nonlinearity for solution-mixed samples. In addition, imaging analysis of the solution-mixed sample depicted heterogeneous dispersion with highly interconnected networks of MWCNT in PS matrix. The interconnected networks of MWCNT developed by solution mixing leads to significantly enhanced EMI shielding performance over melt-mixed nanocomposites containing big clusters of MWCNT in micro-scale but smaller aggregates in nano-scale. Hence, the desired state of dispersion (i.e., heterogeneous dispersion or small agglomerates connected with individual MWCNT) of MWCNT is necessary to achieve maximum EMI shielding performance.

Keywords: Polymer Processing, Nonlinear Viscoelasticity, Rheology, Solution Mixing, Melt Mixing
5.2 Introduction

Multi-walled carbon nanotubes (MWCNTs)/polymer nanocomposites have been widely used due to their outstanding electrical, thermal, and mechanical properties. The superior properties of MWCNTs stem from high aspect ratio of these 1-dimensional nanofillers. However, the final properties of polymer nanocomposites significantly depend on the network structure and dispersion quality of the nanofillers in a polymer media.1-4 MWCNTs and single-walled carbon nanotubes (SWCNTs) are usually synthesized in the form of entangled aggregates and bundles. The dense entanglement of these aggregates would create an obstacle to achieve desired dispersion of the nanotubes in polymer matrices. Hence, achieving a proper dispersion state of these nanofillers in polymer matrices is one of the major challenges in polymer processing industry. Solution mixing and melt mixing techniques are among the most important polymer nanocomposite processing methods used to disperse these nanofillers in polymer matrices. It should be mentioned that, due to complexity of the other methods, e.g., in-situ polymerization and latex approach, great care is required and thus, these methods are not commonly used.

Considering the aforementioned reasons, great efforts have been expended in the recent years to design effective solution mixing and melt mixing methods. Several authors have reported the effect of processing conditions in melt mixing method on dispersion quality of MWCNT and on final properties of nanocomposites.5-7 For instance, in our previous work8 we have compared the electromagnetic interference (EMI) shielding effectiveness of polymer blend nanocomposites fabricated using solution and melt mixing techniques. Significant differences are found in final properties of melt-mixed and solution-mixed nanocomposites.8 Similarly, solution mixing has drawn great attention focusing on the mixing parameters (e.g., sonication method,9 sonication time,10 solvent properties,11 etc.). Song et al.12 studied the effect of state of dispersion of carbon nanotubes in an epoxy resin on rheological, mechanical,
electrical, and thermal properties. Authors achieved better dispersion state by preparation of the samples using solution mixing, leading to better mechanical and electrical properties.

Although solution mixing and melt mixing are the most commonly used approaches in polymer processing in both industry and academia, there is still some debate about the effectiveness and performance of each method. X-ray diffraction (XRD) and transmission electron microscopy (TEM) are simple and effective characterization methods to investigate dispersion of layered nanomaterials in a polymeric matrix. However, complete characterization of nanotube dispersion is a difficult task. Direct techniques such as optical microscopy (OM), scanning electron microscopy (SEM), atomic force microscopy (AFM), and TEM provide limited information of the very small cross-section area. In addition, since the areas are selected by the operator, they do not provide a cumulative representation of the dispersion state of the nanotubes in a given polymer matrix. 13-14 On the other hand, dynamic rheological measurement is a powerful indicator of the dispersion state and microstructure of the nanofillers in the bulk of a filled system. 3, 15-17

The effect of processing condition on linear rheological properties of polymer nanocomposites, using small amplitude oscillatory shear (SAOS), has been widely studied. As an example, Ke et al. 18 studied the effect of solution mixing and melt mixing on linear viscoelastic properties of the MWCNT-based polymer nanocomposites. The authors reported significantly different linear viscoelastic responses between solution-mixed and melt-mixed polymer nanocomposites. However, it should be borne in mind that linear rheology is limited to a narrow strain or stress region, typically low values of strain and stress, and, in the most industrial processing techniques, deformations are large and rapid. Thus, linear rheological measurements cannot provide useful information about the material’s viscoelastic responses exposed to these types of flow. Moreover, different materials with the same linear viscoelastic behavior can have significantly different nonlinear viscoelastic behavior. Hence, an important
question needs to be addressed: How do different processing methods affect the viscoelasticity of the MWCNT-based polymer nanocomposites exposed to real-world large and rapid deformations?

Since oscillatory strain tests have two tunable parameters,\textsuperscript{19} i.e., frequency of the oscillation, which controls the time scale, and the amplitude, which governs the extent of deformation,\textsuperscript{20} they are still the best protocols to probe the nonlinear viscoelastic behavior of the materials. Therefore, the best solution to study the nonlinearity of the polymeric materials is to use the same type of flow as SAOS, but over a broader region of deformation and/or frequency. Rheological tests exploring wider region of amplitude are called large amplitude oscillatory shear (LAOS) tests. LAOS protocol provides valuable information about both inter-cycle (changes between successive oscillations) and intra-cycle (changes in each cycle of oscillation) viscoelastic behavior. Hence, LAOS is a vigorous technique to investigate the materials’ viscoelastic response to nonlinear and transient conditions. In recent years, LAOS tests have been widely used to study the viscoelasticity of polymer solutions,\textsuperscript{21-23} polymer nanocomposites,\textsuperscript{24-25} polymer blends,\textsuperscript{26-29} and polymer hydrogels.\textsuperscript{30} For more information readers can refer to a recent review by Saengow et al.\textsuperscript{31}.

Hence, in contrast to the vast majority of publications concerning the linear viscoelastic properties, this paper focuses on the nonlinear viscoelastic response of MWCNT-based polymer nanocomposites prepared by solution and melt mixing methods. To describe the viscoelastic nonlinearity, rheological responses were classified into two different categories: inter- and intra-cycle. We were able to study nonlinear viscoelastic response using Lissajous–Bowditch plots and quantitative nonlinear viscoelastic parameters.

TEM micrographs of nanocomposites showed the significantly different state of MWCNT dispersion in nanocomposites fabricated by solution and melt mixing strategies. Our findings reveal samples prepared by different mixing method behave differently in nonlinear
viscoelastic region, originating from the quality and the degree of network formation of MWCNT in the polymer matrix. Both TEM and rheological results are in agreement with each other. Finally, the effect of MWCNT dispersion and network formation on EMI shielding performance of nanocomposites is assessed in X-band frequency. It was shown that at a given concentration of MWCNT, owing to networks of highly conductive MWCNT agglomerates and high aspect ratio individual MWCNTs interconnecting the agglomerates, nanocomposites prepared by solution mixing depicted enhanced EMI shielding performance over melt mixed nanocomposites.

5.3 Experimental Section

Materials. Polymer nanocomposites were prepared using PS Styron 666D from Americas Styrenic LLC, and MWCNT (NC 7000) from Nanocyl S.A. (Sambreville, Belgium). Average diameter of NC 7000 is 9.5 nm, average length is 1.5 µm and purity is 90%, according to the manufacturer. For solution-mixed PS/MWCNT nanocomposites, chloroform was used to dissolve PS and to disperse MWCNT.

Sample preparation. PS/MWCNT nanocomposite was prepared with 0.3, 0.5, 1, 2, and 2.7 vol% of MWCNT. During solution mixing, PS was dissolved in chloroform by 30 min of magnetic stirring, and MWCNT was dispersed in chloroform by 30 min of bath sonication. Both of the mixtures were mixed and homogenized for 30 min. After evaporation of the solvent, PS/ MWCNT was dried in vacuum dryer.

Melt-mixed PS/MWCNT samples were prepared at 230 °C and 150 rpm in Alberta Polymer Asymmetric Minimixer (APAM Calgary, AB). The samples were compression molded in Carver compression molder (Carver Inc. Wabash, IN) in a rectangular shape (10 x 23 x 0.8 mm³) at 230 °C. Pressure was maintained at 35 MPa for 10 min. At least three specimens were prepared to measure electromagnetic interference shielding effectiveness (EMI SE).
Characterization. Leica ultramicrotome EM UC6 (Leica Biosystems, Germany) was used to prepare thin sections of compression molded samples with a thickness of 5000nm at room temperature for light microscopy (LM) analysis. Olympus BX60 optical microscope (Olympus Inc, USA) featured with Olympus DP80 camera was used to capture images of thin sections of samples.

Thin sections of 60 to 90 nm thickness were prepared to capture TEM (transmission electron microscope) images of the nanocomposites. The sections were cut by Leica EM UC6 ultra-microtome at room temperature. Tecnai TF20 G2 FEG-TEM (FEI, Hillsboro, Oregon, USA) equipped with Gatan Ultrascan 4000 CCD Camera (Gatan, Pleasanton, California, USA) was used to capture TEM images. Accelerating voltage of 20 kV was applied during imaging.

EMI SE was measured over X-band frequency range (i.e., 8.2 to 12.4 GHz). Network analyzer (ENA) (Agilent Model E5071C), connected to a rectangular wave guide WR-90 was used to capture scattering parameters (S-parameters). EMI SE was calculated using the S-parameters.

The electrical conductivity of the samples was evaluated using Loresta GP resistivity meter, MCP-T610 model (Mitsubishi Chemical Co., Japan) connected to an ESP four-pin probe. The four-pin probe, due to its configuration, eliminates the effect of contact resistance. The applied voltage was 10 V for all the measurements.

Rheological measurements were performed using an Anton-Paar MCR 302 rheometer equipped with a 25 mm diameter parallel plates geometry with a gap size of 0.2 mm. All experiments were carried out at 230 °C. To reach the desired condition (stabilized temperature and nanocomposite morphology), a rest time of 10 min in the rheometer was used after loading the sample. Strain amplitude sweep experiment was carried out on all samples to determine the linear viscoelastic (LVE) regime limit. This test was done over a range of applied strain
amplitudes from $\gamma_0 = 0.1$ to 1000.0 % at an angular frequency of $\omega = 1$ rad/s. Based on the results of this experiment, the strain amplitude of 0.1% was determined to be small enough to keep the deformation in the LVE regime.

To obtain the large amplitude oscillatory shear (LAOS) results, the rheometer was placed in a rigid and mechanically stable environment to minimize any mechanical noise. To obtain last full waveform of shear stress and strain, the material was strained at a constant frequency and a constant amplitude. LAOS data were collected after 5-6 cycles for each strain amplitude.

5.4 Results and Discussion

5.4.1 MWCNT dispersion and distribution

Imaging techniques (e.g., TEM, OM, and SEM) are the most common direct characterization methods to study the dispersion state of nanofillers in a polymer media. Figure 5-1 shows the dispersion and distribution of PS/2.0 vol % MWCNT prepared by melt mixing and solution mixing processes in micro- and nano-scale. Hence, TEM was employed to characterize agglomerate sizes below the LM limit (nano-dispersion), where individually dispersed CNT can be imaged.

Shear applied by solution mixing and melt mixing is different, so dispersion of MWCNT in polymer matrix would be different for each case. Nanocomposites with the same composition, but prepared by different processing techniques exhibit dissimilar dispersion and distribution of nanofiller. In this work, we found that 2 vol.% of MWCNT was dispersed in PS with a number of agglomerates, in both melt-mixed and solution-mixed samples in both micro- and nano-scale. The number and size of agglomerates in solution-mixed sample was higher than in melt-mixed sample in nano-scale as corroborated by TEM images. This observation contradicts findings by Ke et al.\textsuperscript{18}. They showed that solution mixing led to better dispersion of MWCNT in PVDF than melt mixing. This contradictory finding is not unusual because
dispersion attained by solution mixing is always a function of amount of solvent, solvent-polymer interaction, concentration of nanofiller and strength of ultrasound wave. However, based on light microscopy images, the micro-dispersion quality of the solution-mixed sample is better as this sample consists of higher number of smaller sized agglomerates connected with each other by higher number of individual MWCNT which was verified by the darker color of the LM image.

Moreover, in our case, MWCNT was found to form a segregated network-like structure in nano-scale in the polymer matrix of solution-mixed sample, which was not seen in the TEM images of melt-mixed sample. TEM images of nanocomposites with 0.5 vol.% MWCNT shown in Figure S1 of Appendix C were also investigated, to check if similar nano-dispersion (segregated structure) to 2.0 vol.% was obtained. Solution-mixed sample with 0.5 vol.% MWCNT showed similar but less dense network of MWCNT in PS/2.0 vol.% MWCNT, which is attributed to the lower concentration of MWCNT. Segregated network structure in nano-scale and less agglomeration in micro-scale both lead to better electrical properties in polymer nanocomposites. Gelves et. al.\textsuperscript{32} obtained advanced electrical properties due to segregated network-like structure of CuNW in PS matrix by miscible solvent mixing and precipitation method (MSMP). The characteristics of microstructures of conductive nanofillers, e.g., dispersion state, dictates the functional properties, e.g., EMI shielding performance, of resulting nanocomposites. Thus, there is significant motivation to investigate the EMI shielding performance of our polymer nanocomposites to further study the network/microstructure of melt-mixed and solution-mixed samples.
Figure 5-1: Dispersion and segregated network formation of MWCNT in PS/2.0 vol% MWCNT nanocomposites: (a) melt mixed and, (b) solution mixed. (a₁) and, (b₁) are high-resolution images of the respective nanocomposites, showing MWCNT with more clarity. The hexagons show the void parts, generated by the segregated distribution of MWCNT in solution-mixed sample in nanoscale. The white arrows indicate MWCNT. (c) and (d) LM images of microtomed melt-mixed and solution-mixed PS/2.0 vol% MWCNT nanocomposites, respectively.

5.4.2 Electromagnetic interference shielding

Electromagnetic interference shielding materials are necessary to protect human health and to ensure the best performance of electronic devices. In general, conductive materials act as efficient EMI shields. In this context, polymer nanocomposites containing conductive fillers have recently gained a great deal of interest. 33 It has been reported in several studies that an enhanced network of conductive nanofiller provides higher EMI shielding effectiveness (SE) in polymer nanocomposites. 32, 34-35 Apart from enhanced electrical conductivity, the EMI SE also scales with higher degree of interconnected networks of conductive fillers. Thus, EMI SE of polymer nanocomposites has been selected as an indirect tool to investigate the quality of
network of MWCNT in the polymer matrix. Figure 5-2 shows EMI SE of the PS/MWCNT nanocomposites prepared by solution mixing and melt mixing as a function of MWCNT concentration in the nanocomposites. Nanocomposites with higher concentration of MWCNT showed higher EMI SE, which can be attributed to enhanced MWCNT-MWCNT contacts, associated with higher concentration of MWCNT. It is observed that solution-mixed samples exhibited higher EMI shielding performance than melt-mixed samples, at any given concentration of MWCNT. This suggests enhanced network formation of MWCNT in solution-mixed samples over melt-mixed samples, which is in complete agreement with LM and TEM images.

Thus, it can be concluded that nano-scaled segregated network conjugated with smaller sized clusters of MWCNT in micro-scale in solution-mixed samples favored electrical (see electrical conductivity results in Figure S2 of Appendix C) and EMI shielding properties more than the network obtained in melt-mixed samples. Since MWCNTs are mostly confined within bigger agglomerates, availability of MWCNTs in nanoscale is comparatively less and apparently nano-dispersion is better (see TEM images in Figure 5-1(a)) in melt-mixed samples. However, this type of dispersion reduces the availability of MWCNTs to construct efficient conductive network. On the other hand, PS chains have better wetting effect of MWCNTs at
the presence of solvent, which results in better micro-dispersion (smaller sized clusters, see Figure 5-1(d)) and favorable nano-dispersion (see Figure 5-1(b)) of MWCNTs in solution mixed sample as compared to melt mixed samples. Therefore, more MWCNTs can participate in formation of conductive network and facilitate better electrical properties for samples prepared by solution mixing method.

In addition, as observed from TEM micrographs, the hexagonal networks of MWCNT formed in solution-mixed samples in nano-scale act as microwave absorbing pockets, where microwaves scatter multiple times from highly conductive hexagon walls, which are constructed by the smaller agglomerates of MWCNTs. Moreover, in the case of solution-mixed samples, the highly conductive smaller agglomerates of MWCNTs were interconnected through individual MWCNTs (corroborated by LM image) leading to numerous conductive paths for dielectric loss in the materials, and hence, showed enhanced EMI SE. Therefore, a desired or optimum state of filler dispersion is necessary, depending on the final application of the material.

For instance, the solution-mixed and melt-mixed nanocomposites containing 2.7 vol% MWCNT depicted EMI SE of 22 and 15 dB, respectively. For most of the commercial applications, a minimum EMI SE of 20 dB is desired, equivalent to blocking 99% of incoming microwaves. The development of network structure of MWCNT in PS nanocomposites will be discussed in detail via rheological analysis using SAOS and LAOS experiments in subsequent sections.

5.4.3 Linear Rheology (SAOS)

Frequency sweep. The linear viscoelastic responses of the samples were investigated and the results are presented in Supporting Information (see Figure S3 of Appendix C and the corresponding discussion). Based on these results, both solution-mixed and melt-mixed samples have predominantly elastic character even at low MWCNT loadings. However, the
solid-like behavior is more pronounced for solution-mixed samples. These results will be further used in order to interpret the nonlinear viscoelastic response of the nanocomposite samples.

Moreover, based on Figure S8 of Appendix C, melt-mixing processing has negligible detrimental effect on rheological behavior of the PS matrix (i.e., storage modulus decreased from 75 to 40 Pa after mastication) and, thus, the dramatic differences (more than one order of magnitude) in rheological response of melt-mixed (storage modulus $G'_s=1.3\times10^3$ Pa) and solution-mixed (storage modulus $G'_s=1.6\times10^5$ Pa) samples mainly originate from nanotube’s microstructural differences between these nanocomposite samples.

5.4.4 Nonlinear rheology (LAOS)

Strain amplitude sweep test (inter-cycle viscoelastic properties). In this section, strain sweep experiments were performed to link the inter-cycle nonlinear viscoelastic responses of the samples obtained under oscillatory shear flow to MWCNT network structure. Figure 5-3 shows the amplitude dependence of viscoelastic behavior of MWCNT/PS nanocomposites containing 0.5 and 2.0 vol.% nanotubes prepared by different mixing methods. At strain amplitudes smaller than critical strain amplitude (i.e., strain at which linear to nonlinear viscoelastic transition occurs, highlighted by star symbols in Figure 5-3), the viscoelastic moduli are independent of the applied deformation, demonstrating linear viscoelastic (LVE) region. The larger $G'$ compared to that for loss modulus $G''$ in solution-mixed nanocomposite containing 0.5 vol.% MWCNT in the LVE region indicates an elastic dominant response, which is in line with SAOS results (see Figure S3 of Appendix C). However, the $G'' > G'$ condition for melt-mixed PS/0.5 vol.% MWCNT, indicates a viscous dominant response. Increasing the content of filler leads to increase in both moduli ($G''$ and $G'$) and samples with 2.0 vol.% MWCNT exhibit a significantly flocculated gel behavior. At this loading of MWCNT, $G'$ of the solution-mixed nanocomposite is more than one order of magnitude larger.
than $G'$ of the melt-mixed nanocomposite in LVE framework. This means that solution-mixed samples feature a better (stronger) network structure of MWCNTs, which agrees with imaging and electrical analyses.

Exceeding the limit of linear viscoelasticity, $G'$ gradually decreases and samples with elastic dominant response exhibit a crossover point (strain amplitude at which $G''$ becomes greater than $G'$, which is indication of transition from elastic behavior to flow). The decrease in the $G'$ values of the nanocomposite samples is thought to be associated with the nanofiller network rupture and orientation of the nanofillers parallel to flow direction.\textsuperscript{24, 37} Since the solution-mixed samples has a stronger and a more rigid nanofiller network compare to the melt-

\[\text{Figure 5-3: Oscillatory amplitude sweep response of PS/MWCNT nanocomposites containing (a) and (b) 0.5vol.\% and (c) and (d) 2.0vol.\% of carbon nanotubes for strain amplitudes of $\gamma_0=0.1$-1000\% at an angular frequency of $\omega=1$ rad/s using a parallel-plate geometry at a gap-size of 0.2 mm at 230 °C. Open symbols represent loss modulus ($G''$) and solid symbols represent storage modulus ($G'$). The star symbols show the critical strain amplitude (linear to nonlinear transition).}\]
mixed samples, their structures break down at smaller strain amplitudes. That is, both critical strain amplitude and crossover point shifted to smaller strain amplitudes for solution-mixed nanocomposites. After the crossover strain amplitude, both moduli show a dramatic decrease. The monotonic strain-induced decrease in the moduli of the systems after the crossover strain amplitude indicates inter-cycle strain-thinning behavior for both solution-mixed and melt-mixed samples.

In summary, regardless of the mixing method, the nanocomposites samples follow the same inter-cycle nonlinear pattern (strain-thinning) at large deformations. However, mixing method affected the extent of the inter-cycle viscoelastic behavior. In this regard, nanocomposite samples prepared by different mixing methods demonstrated dissimilar $G'$ and $G''$ values in LVE region, different critical strain amplitudes, different crossover points, and different rates of inter-cycle nonlinearity.

Despite the fact that both solution-mixed and melt-mixed samples show a same type of inter-cycle nonlinear behavior (strain-thinning), they showed different intra-cycle nonlinearity in both medium and large amplitude regions. In the next sections, to obtain the true impact of mixing method on nanocomposites’ nonlinear viscoelastic properties, we will study intra-cycle response of samples using Lissajous-Bowditch plots (see Figures S6 and S7 and the corresponding discussion in Appendix C) and quantitative nonlinear viscoelastic parameters.

**Nonlinear viscoelastic parameters.** Figure 5-4 (a), (b), and (c) show local dynamic viscosities (minimum strain rate viscosity $\eta'_M$ and large strain rate viscosity $\eta'_L$) and Figure 5-4 (d), (e), and (f) demonstrate local elastic measures (minimum strain modulus $G'_M$ and large strain modulus $G'_L$). Ewoldt et al. used these nonlinear local parameters to develop dimensionless indices to define the type of intra-
cycle nonlinearity. In this context, strain-stiffening ratio \( S \equiv \frac{G_L' - G_M'}{G_L'} \) can be used to describe intra-cycle elastic nonlinearity. Table 1 summarizes elastic nonlinear parameters and provides a guideline for recognizing the type of elastic nonlinearity based on each of the defined parameters.

Table 5-1: Characterizing elastic nonlinearity in response to imposed LAOS deformation\(^{38}\)

<table>
<thead>
<tr>
<th>Elastic parameters</th>
<th>Inter-cycle</th>
<th>Intra-cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Both ( G_M' ) and ( G_L' ) increase by increasing ( \gamma_0 )</td>
<td>Inter-cycle strain stiffening</td>
<td>-</td>
</tr>
<tr>
<td>Both ( G_M' ) and ( G_L' ) decrease by increasing ( \gamma_0 )</td>
<td>Inter-cycle strain softening</td>
<td>-</td>
</tr>
<tr>
<td>( S &gt; 0 ) at each strain</td>
<td>-</td>
<td>Intra-cycle strain stiffening</td>
</tr>
<tr>
<td>( S = 0 )</td>
<td>-</td>
<td>Linear elastic behavior</td>
</tr>
<tr>
<td>( S &lt; 0 ) at each strain</td>
<td>-</td>
<td>Intra-cycle strain softening</td>
</tr>
</tbody>
</table>

Shear-thickening ratio \( T \equiv \frac{\eta_L' - \eta_M'}{\eta_L'} \) characterizes intra-cycle dissipative (viscous) nonlinearity (see Table 2). See Table 2 for viscous nonlinear parameters.

Table 5-2 Characterizing viscous nonlinearity in response to imposed LAOS deformation\(^{38}\)

<table>
<thead>
<tr>
<th>Viscous parameters</th>
<th>Inter-cycle</th>
<th>Intra-cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Both ( \eta_M' ) and ( \eta_L' ) increase by increasing ( \gamma_0 )</td>
<td>Inter-cycle shear thickening</td>
<td>-</td>
</tr>
<tr>
<td>Both ( \eta_M' ) and ( \eta_L' ) decrease by increasing ( \gamma_0 )</td>
<td>Inter-cycle shear thinning</td>
<td>-</td>
</tr>
<tr>
<td>( T &gt; 0 ) at each strain</td>
<td>-</td>
<td>Intra-cycle shear thickening</td>
</tr>
<tr>
<td>( T = 0 )</td>
<td>-</td>
<td>Linear elastic behavior</td>
</tr>
<tr>
<td>( T &lt; 0 ) at each strain</td>
<td>-</td>
<td>Intra-cycle shear thinning</td>
</tr>
</tbody>
</table>

Based on Figure 5-4, in LVR, associated with small deformations, both \( G_L' \) and \( G_M' \) converge to the linear elastic modulus \( G' \), i.e., \( G_L' = G_M' = G' \). Thus, \( S \) index is roughly zero, indicative of no elastic intra-cycle nonlinearities. By increasing the strain amplitude, \( G_L' \) and \( G_M' \) values drop. The decreasing trend of \( G_M' \) is faster than \( G_L' \), resulting in the departure of the \( S \) index from zero values to positive values. The positive \( S \) in deep nonlinear region indicates that intra-cycle elastic nonlinearity is strain-stiffening behavior. This behavior for neat PS can be attributed to strain induced stretching of the polymer chains extending into the non-Gaussian regime.\(^{39}\) The same intra-cycle strain-stiffening behavior was observed for neat Poly(vinylidene fluoride) (PVDF) polymer in our previous work.\(^{24}\) However, regardless of
mixing method, incorporation of MWCNT into PS matrix influences the intra-cycle elastic nonlinearity. That is, the onset of intra-cycle elastic nonlinearity (initial departure of $S$ index from zero value) decreases to smaller strain amplitudes (which is in agreement with the results of Figure 5-3). As mentioned earlier, this can be attributed to the higher sensitivity of the rigid MWCNT network structure to the applied deformation, which not only affects the inter-cycle properties, but also impacts the intra-cycle properties. Moreover, the value of the $S$ index at maximum deformation ($\gamma_0=100\%$) decreases from 100% for pure PS to 80% and 68% for solution-mixed and melt-mixed sample, respectively. This is related to less chain stretching due to the load bearing performance of MWCNT network and shear stress dissipation by MWCNT network rupture and orientation of the individual MWCNT in flow direction.
Figure 5-4 (a) shows $\eta'_M$ and $\eta'_L$ of neat PS. $\eta'_M - \eta'_L$ and their values are constant up to strain amplitude of 100%, indicating that all the viscous nonlinear contributions are negligible for PS matrix. The decrease in both $\eta'_M$ and $\eta'_L$ after strain amplitude of 100% reveals that the viscous inter-cycle nonlinearity of pure PS is shear-thinning behavior. Comparing the rate of the decrease in $\eta'_M$ and $\eta'_L$ of the neat PS to define the type of intra-cycle nonlinearity beyond the LVE limit is challenging with naked eyes. However, the $T$ index of neat PS, which is plotted in Figure 5-4 (g), eases analyzing the viscous intra-cycle nonlinear viscoelasticity. Based on the results of Figure 5-4 (g), the negative $T$ index in LAOS region indicates that PS matrix follows an intra-cycle shear-thinning behavior. This behavior is because of the chain slippage and polymer network junction (e.g., entanglement) loss at high shear rates.

Figure 5-4: (a), (b), and (c) local viscosities: minimum strain rate viscosity $\eta'_M$ and large strain rate viscosity $\eta'_L$; (d), (e), and (f) local elastic measures: minimum strain modulus $G'_M$ and large strain modulus $G'_L$; (g), (h), and (i) intra-cycle viscoelastic parameters: strain-stiffening ratio ($S$) and shear-thickening ratio ($T$). Data have been obtained at angular frequency of $\omega = 1$ rad/s using a parallel-plate geometry at 230 °C for PS/2.0 vol.% MWCNT. See Figures S2 and S3 for the same results at MWNCT concentrations of 0.5 and 1.0 vol.%, respectively.
Incorporation of the MWCNT into the PS matrix dramatically changes the intra-cycle viscous behavior of nanocomposites. This change was not identifiable in Figure 5-3 (presenting the lumped viscoelastic functions providing an overall measure of inter-cycle nonlinearity). That is, a strong intra-cycle shear-thickening behavior occurs for solution-mixed sample in medium amplitude oscillatory shear (MAOS) region. This behavior is less pronounced for melt-mixed sample and starts at larger strain amplitude. Figure S5 of Appendix C shows the nonlinear parameters for polymer nanocomposites containing 1.0 vol.% MWCNT. Interestingly, there is no intra-cycle shear-thickening nonlinearity for melt-mixed samples containing 1.0 vol.% or lower concentrations of MWCNTs (i.e., similar behavior was observed for PS/0.5 vol.% MWCNT, see Figure S4 of Appendix C). Hence, changing the mixing method have a considerable impact on viscous intra-cycle nonlinearity of nanocomposites. The observed intra-cycle shear thickening behavior in intermediate strain amplitude region can be attributed to shear-induced network densification process during the transition into the LAOS region.\textsuperscript{22, 40-41} This dissipative feature can potentially stem from compression of particle-rich domains, leading to drainage and expulsion of interstitial fluid within the fractal cluster.\textsuperscript{23, 25} In solution mixing process, the polymer macromolecules are able to diffuse and migrate into the dense MWCNT clusters; this is due to better wetting ability of PS chains in the presence of solvent. Therefore, the clusters of solution-mixed sample are less compact as they contain PS chains and this is observed in LM images as they are lighter compared to melt-mixed clusters. So, in solution-mixed samples, with higher number of micro- and nano-scale agglomerates filled with PS chains, the densification process, is more pronounced compared to melt-mixed samples and leads to MAOS shear-thickening behavior.

$T$ index decreases after the observed increasing trend in MAOS region. By further increase in the applied deformation the sign of the $T$ changes from positive to negative values, signaling a conversion from intra-cycle shear-thickening to intra-cycle shear-thinning.
behavior. The intra-cycle shear-thinning behavior is more pronounced for nanocomposites compared to neat PS. The significant shear-thinning nonlinearity of the nanocomposite samples can be correlated to the MWCNT network disruption and orientation of the MWCNT in extremely large shear rates associated with large deformations. Moreover, $T$ index of the samples prepared by solution mixing approach gets negative values with steeper slope (see Figures S2 and S3 of Appendix C for the same behavior for other concentrations of MWCNT). Hence, the absolute value of $T$ index of solution-mixed polymer nanocomposites is much larger than melt-mixed samples at the largest deformation, indicating a stronger intra-cycle shear-thinning behavior for solution-mixed samples. This is in agreement with our previous work that we observed higher intra-cycle shear-thinning behavior by improving the dispersion quality of MWCNTs (for more information readers are referred to our previous work).

In this section, we were able to achieve viscoelastic data not accessible to linear rheological experiments or the lumped data provided by routine strain amplitude tests. This shows vigorous sensitivity of the local viscoelastic measures and intra-cycle parameters to any changes in the microstructure. Nonlinear viscoelastic behavior of the samples has been also qualitatively expounded assisting Lissajous-Bowditch plots (see Figure S6 and S7 and the corresponding discussion in Appendix C).

5.5 Conclusions

This study shows that the results of large amplitude oscillatory shear (LAOS) techniques provide us complementary information about: (i) the effect of the mixing techniques on network formation of 1-D nanofillers within a polymer matrix, and (ii) exploration of intra-cycle nonlinear viscoelastic behavior of polymer nanocomposites. To achieve this, MWCNT-based polymer nanocomposites were prepared by two approaches, melt mixing and solution mixing methods, at different concentrations of the MWCNT up 2.7 vol.%. The network structures of the samples were initially investigated using imaging techniques and electrical
measurements. It was shown that solution-mixed samples showed better EMI shielding performance. This can be attributed to existence of the MWCNT clusters in nano-scale, which are connected to each other via individually dispersed MWCNT, as corroborated utilizing imaging techniques. This signals that presence of nano-scale clusters of the conductive nanofillers improves the electrical performance of nanocomposites. In line with microwave properties, solution-mixed samples showed higher storage and loss moduli in linear viscoelastic framework, signifying a more solid-like behavior from rheological point of view.

Viscoelasticity of the solution-mixed nanocomposites also featured higher nonlinearity, in both medium- and large amplitude oscillatory shear (MAOS and LAOS) regions. For instance, an extreme intra-cycle shear-thickening behavior occurred in MAOS region for PS/1.0 vol.% solution-mixed sample, while no intra-cycle nonlinearity was observed for its melt-mixed counterpart. Additionally, the intra-cycle nonlinearity of solution-mixed samples in LAOS region was accompanied by a self-intersection in viscous projection of Lissajous-Bowditch loops. These data verify the intense sensitivity of the nonlinear viscoelasticity to the microstructure of polymer nanocomposites. Hence, LAOS provides us with the unique opportunity to investigate and link the macro-scale nonlinear mechanical response of prepared nanocomposites to nano-scale structural features of nanofillers’ network.

5.6 Acknowledgments

Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) is highly appreciated.

5.7 References


Chapter 6 - On the Viscoelastic Response of Covalently Cross-linked Gelatin Methacryloyl (GelMA) Hydrogel under Large Shear Deformations**

Presentation of the Article:

In this work, for the first time we studied the nonlinear viscoelastic behavior of covalently cross-linked hydrogels employing a novel technique to eliminate any error arising from wall-slip. The results of the current work show that viscoelastic data of the hydrogels are highly affiliated with will-slip error. To solve this problem, we chemically bonded the hydrogels to glass slides followed by attaching the glass slides to the rheometers’ plates using a double-sided tape. Using this approach, huge differences in type of the viscoelastic behavior and values of nonlinear parameters of attached and unattached samples were observed. Moreover, this technique enabled us to report the true inter- and intra-cycle nonlinear behavior of the hydrogels with great accuracy. In addition, the effect of concentration of polymers on nonlinearity of the hydrogels has been investigated in this article. The correlation between the microstructure and viscoelastic properties under large deformations provides further guidance for fabrication of high-performance hydrogels with precisely controllable microstructures and mechanical behaviors.

Authors’ contributions:

I organized and wrote the paper. I performed rheological measurements. Mr. Janmaleki helped with preparation and characterization of the samples. Dr. Sanati-Nezhad helped with analyzing the materials’ characterization and Prof. Sundararaj supervised the whole work.

**Journal of Mechanical Behavior of Biomedical Materials (under review)**
On the Viscoelastic Response of Covalently Cross-linked Gelatin Methacryloyl (GelMA) Hydrogel under Large Shear Deformations

Milad Kamkar,a† Mohsen Janmaleki,b† Amir Sanati-Nezhad,c Uttandaraman Sundararaj*a*

a Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr NW, Calgary, Alberta T2N 1N4 Canada
b BioMEMS and Bioinspired Microfluidic Laboratory, Biomedical Engineering Graduate Program, University of Calgary, Calgary, Alberta T2N1N4, Canada
c BioMEMS and Bioinspired Microfluidic Laboratory, Department of Mechanical and Manufacturing Engineering, University of Calgary, Calgary, Alberta T2N1N4, Canada
† M.K and M.J made equal contributions to this work. *Corresponding Authors: E-mail: u.sundararaj@ucalgary.ca (Uttandaraman Sundararaj)

Abstract
Gelatin-based hydrogels have been widely used in tissue engineering, three-dimensional cell culture, drug delivery, and cell therapy. Mechanical behavior of hydrogels together with their chemical properties determine the functionality and efficacy of the final products. With respect to the mechanical behavior of hydrogel biomaterials, the vast majority of publications have reported linear viscoelastic response. However, in practical conditions in body, these materials experience large deformations beyond the linear viscoelastic limit. Herein, to mimic practical conditions and to evaluate the mechanical response of the hydrogels subjected to large deformations, we report inter- and intra-cycle nonlinear viscoelastic behavior of gelatin methacryloyl (GelMA) hydrogel with different concentrations of the hydrogel precursor (10 to 20% (w/v)) under large amplitude oscillatory shear deformation. To achieve this, we propose a novel technique by chemically bonding the hydrogels to treated glass-slides which are attached to the oscillating metal plates using double-sided tape to alleviate any error arising from wall-slip in rheological measurements. Employing this method, attached and unattached hydrogels showed different type inter-cycle viscoelastic responses at large amplitudes and values of viscoelastic parameters improved in accuracy by an order of magnitude. Moreover, the results show that the elastic character of covalently cross-linked hydrogels in large deformations obeys a nonlinear force-extension law and the viscous intra-cycle nonlinearity in moderate amplitudes stems from dual cross-linked nature of GelMA hydrogel. It was also shown that mechanical parameters can be tuned by concentration of the hydrogel precursor, i.e., stress at break increased from 2.6 to 7.1kPa, strain at break decreased from $\gamma_0=100$ to 70%, and the onset of inter-cycle nonlinearity shifted from $\gamma_0=50$ to 20% upon increasing the concentration of the hydrogel precursor. These insights have important implications for the rational development of hydrogel-based biomaterials for designing of biocompatible scaffolds in tissue engineering applications.

Keywords: Hydrogel, Rheology, Nonlinear viscoelasticity, Wall-slip.
6.1 Introduction

Hydrogels are cross-linked polymeric networks with the capability to retain a large volume fraction of water. Hydrophilic functional groups on the polymeric backbone enable the structure to swell, while the cross-linked network minimizes dissolution into water \(^1\). Biocompatible hydrogels with tunable mechanical and biological properties have potential applications in regenerative medicine such as 3D hepatic tissue \(^2\) and vascular tissue reconstructions \(^3\). Hydrogels have been also used for organ-on-chip platforms, tissue adhesives, drug delivery, and wound healing \(^4\). Gelatin methacryloyl (GelMA) hydrogel has biophysical and biochemical properties similar to native extracellular matrix (ECM) and thus, provides appropriate microenvironment for cell attachment, proliferation, spreading, and differentiation \(^5\). GelMA hydrogel has been extensively used as a functional biomaterial in engineering of different soft tissues such as vascular tissue \(^6\), ligaments \(^7\), tendons \(^7\), muscles \(^8\), and articular cartilage \(^9\). These tissues are responsible for connecting, supporting, and protecting other organs. With fiber-reinforced structures, these tissues can undergo large deformations. The constituting macromolecules, like collagen fibers, enable soft tissues to behave anisotropically with viscoelastic behavior. To get the highest benefit from the hydrogels in the engineering of soft tissues, it is essential to have a deep knowledge about their behavior under different mechanical conditions \(^10\).
Dynamic rheometry is a powerful tool for investigating the mechanical behavior and microstructure of biomaterials. For instance, rheology has been widely used to probe microstructural changes during the gelation of hydrogels. Salimi-Kenari et al. used linear viscoelastic response of a hydrogel for gel point determination. In another study, Moura et al. studied gel properties of a cured cross-linked chitosan hydrogel at different concentrations of genipin using linear viscoelastic measures. Authors correlated the linear viscoelastic parameters, e.g., storage modulus, to the microstructural parameters of the cured systems, e.g., length of the flexible polymer chains between the cross-links. The authors also argued that chemically cross-linked hydrogels have advantages over physically cross-linked hydrogels.

Yue et al. showed the diverse application of GelMA hydrogels as a tunable biomaterial for tissue engineering. Such diversity in their applications requires them to have a range of mechanical behaviors. Their mechanical properties not only regulate biological behavior of the embedded cells but also determine the final properties of the developed tissues. Although there are numerous reports on mechanical response of the hydrogels, researchers have mainly investigated the properties under ultra-small deformations. For instant, Fu et al. have studied the physical properties of gelatin-based hydrogels using linear rheological approaches. They were able to distinguish the network structure of covalently and physically cross-linked gelatin hydrogels by comparing their linear viscoelastic parameters. However, in practical situations, the designed hydrogels experience large and rapid deformations, outside the linear viscoelastic region.

Hence, it is of great importance to study the nonlinear viscoelastic behavior of hydrogels. Unlike current literature, evaluating viscoelasticity of the hydrogels in linear framework, we study the nonlinear viscoelastic response of a gelatin-based hydrogel using large amplitude oscillatory shear (LAOS) mode. Over the last decade, LAOS has been extensively employed to study nonlinear viscoelasticity in a variety of systems, such as
polymer solutions \textsuperscript{15}, polymer nanocomposites \textsuperscript{16-17}, and polymer hydrogels \textsuperscript{18-19}. Different approaches can be employed to formulated materials behavior under large deformations.\textsuperscript{20-22} Herein, we adopted a new method introduced by Ewoldt et al. in 2010 for characterizing nonlinear viscoelasticity in large amplitude shear deformations.\textsuperscript{23} Using this method, we were able to study both inter-cycle and intra-cycle nonlinearity (see background section in Supporting Information, Appendix D). Thus, this work will guide the development and improvement of new hydrogels that can mimic the unique viscoelastic properties of native extracellular matrix.

6.2 Sample preparation and characterization.

6.2.1 GelMA hydrogel preparation.

GelMA hydrogel was prepared according to a widely used protocol\textsuperscript{13}. Scheme 6-1 shows the procedure of GelMA hydrogel preparation. Gelatin powder was first dissolved in phosphate buffered saline (PBS) (pH 7.4) in 10\% (w/v). For each gram of gelatin, 0.6g of methacrylic anhydride (Aldrich 27668 94\%) was added in a drop wise manner over a 3 hours period. Meanwhile, the solution was vigorously stirred and kept at a temperature of 50°C. The methacrylation reaction was quenched by adding pre-warmed PBS with the same volume of the solution. Then it was dialyzed against ultra-pure DI water using a 12-14 KD filter for 4 days. After removal of impurities, the solution was snap-frozen in liquid nitrogen. The product was lyophilized in a freeze dryer for 5 days. GelMA hydrogel was prepared by dissolving GelMA precursor in warm PBS at 10, 15, and 20\% (w/v) concentrations. A water-soluble photo-initiator (Irgacure 2959) was used at a concentration of 5mg/mL to initiate crosslinking under UV exposure (254nm, 10mW/cm\textsuperscript{2}, and 2min). Figure S1 of Appendix D and the corresponding discussion show the degree of methacrylation of hydrogels.
Scheme 6-1: Hydrogel preparation procedure. GelMA was prepared by photo-crosslinking of methacrylated gelatin. GelMA precursor solution was added on a TMSPMA treated glass coverslip. The thickness of the hydrogel was controlled by the thickness of a PDMS slab enclosing GelMA hydrogel (it is not illustrated for graphical purposes).

6.2.2 Bonding GelMA hydrogel to glass slides.

Mechanical evaluation of the hydrogels requires reliable linkage of the samples to the rheometer’s plates. The presence of wall-slip at the interface between metal plate and the polymeric system is known to greatly affect the apparent rheological response of polymers. Therefore, it is necessary to alleviate any possible errors arising from slippage at the polymer-plates interfaces. Regular adhesives do not prevent slippage given the fact that the GelMA hydrogel retains above 80wt% water. Hence, unlike the work reported in the literature that did not consider wall-slip for rheological measurements of hydrogels containing high amount of water, we propose a novel method in this work to reduce the wall-slip. To minimize wall slip, hydrogel samples were chemically bonded to two thin circular glass slides using 3-(Trimethoxysilyl) propyl methacrylate (TMSPMA) (see Scheme 6-1 and Figure 6-1). Following the immersion in 1 M NaOH solution for 1 hour, the slides were washed thoroughly using DI water. Following the rinsing of the slides with ethanol and air drying, the glass slides were treated by oxygen plasma (200mTorr pressure, 30W) for 2min. Then, the slides were immersed in the dilution of 0.5% TMSPMA in solution of 97% ethanol and 3.0% acetic acid.
(10.0%) for 10min. The treated slides were washed again with ethanol and air-dried. The slides were then incubated for 10min at 80°C in a sealed oven to anneal the TMSPMA coated layer. Figure S2 of Appendix D shows the surface coverage of the glass slides by TMSPMA.

An in-house prepared polydimethylsiloxane (PDMS) gasket was used to fix the thickness and boundaries of the GelMA hydrogel. The GelMA solution was added within the gasket while it was seated on the bottom slide. After placing the treated glass slide at the top, the bonded layers were exposed to UV radiation (254nm, 10mW/cm²) for 2min to cure the hydrogel. Available superficial hydroxyl group on the surface of the top and bottom glass slides made the hydrogel bond to glass slides while curing. The sandwich samples were used for rheological characterization by attaching the glass slides to the rheometer’s plates using double-sided tape (see Figure 6-1). Based on our observations, the bonding between hydrogel and glass slide is strong enough to prevent slip. Therefore, all the ruptures occurred in the bulk of the hydrogels, and no detachment was observed at the interface of hydrogel-glass slide (see Figure S13 of Appendix D). Dramatic differences in rheological behavior of these two samples is observable which most likely stem from wall-slip phenomenon at the interface of hydrogel-metal plate. Hence, this method inhibits potential errors arising from the wall-slip.

Figure 6-1: Side view for specimen between rheometer’s plates (parallel-plate geometry).
6.2.3 Rheological measurements.

Rheological measurements were performed using an Anton-Paar MCR 302 rheometer equipped with 25mm diameter parallel plates with a fixed gap size (based on samples thickness). All experiments were carried out at room temperature. Strain amplitude sweep experiments (from strain amplitude of $\gamma_0 = 0.1\%$ to yielding point of the samples) were performed at an angular frequency of 1 rad/s on all the samples to determine the linear viscoelastic region (LVR). Based on the results of this experiment, strain amplitude of $\gamma_0 = 1\%$ was determined to be small enough to keep the deformation in the linear viscoelastic regime.

Before running experiments, the gap-size has been zeroed with glass slides attached to the plates. Additionally, it should be also mentioned that the inertia calibration was done before each run with a glass slide attached to upper plate of parallel plate geometry.

To obtain the LAOS results, the rheometer was placed in a rigid and mechanically stable environment to minimize any mechanical noise. LAOS data were collected after 5-6 cycles for each strain amplitude. We carried out rheological tests for several samples of each hydrogel, and the average values of rheological measurements are presented.

6.2.4 Scanning electron microscopic (SEM).

SEM micrographs were obtained using Philips XL30 SEM. Samples were freeze-dried overnight and imaged the day after. ImageJ software was used to estimate porosity of the hydrogels.

6.3 Results and discussion

6.3.1 SEM characterization.

Figure 6-2 depicts SEM micrographs of hydrogels. The results of Figure 6-2 clearly show that increasing the GelMA concentration decreases the mesh size of the structure. Figure 6-2 shows that the pores of GelMA hydrogel have a uniform distribution in 10% (w/v) GelMA concentration with an average pore size of 48.5μm and standard deviation (SD) of 21μm.
Higher concentrations of the hydrogel non-surprisingly leads to smaller average ± SD pore size of \(33.6\pm19\mu m\) and \(27.2\pm16\mu m\) for 15% (w/v) and 20% (w/v) GelMA concentrations, respectively.

![Scanning electron microscopic (SEM) micrographs illustrating the structure of GelMA hydrogels at different GelMA concentrations.](image)

**6.3.2 Linear viscoelastic elastic response.**

The linear viscoelastic response of the hydrogels was investigated, and the results are presented in Supporting Information (see Figure S4 in Appendix D and the corresponding discussion). Based on these results, GelMA hydrogels has predominantly elastic character. It was also shown that the intensified elastic-like behavior stems from dual cross-linked (DC) (featuring both physical and covalent cross-links) network structure of the GelMA hydrogels. These results will be further used to interpret the nonlinear viscoelastic response of the GelMA hydrogels.

**6.3.3 Strain amplitude sweep test.**

To probe the mechanical behavior of gelatin-based hydrogel at large deformations, oscillatory strain amplitude sweep tests were performed at strain amplitudes ranging from \(\gamma_0 = 0.1\%\) to yielding (rupture) strain of the hydrogels at a fixed frequency of 1 rad/s. Figure 6-3 shows the dynamic moduli (storage modulus \(G'\) and loss modulus \(G''\)) as a function of strain amplitude. The data obtained based on Figure 6-3 reveals that \(G'\) exhibits a plateau (modulus is constant regardless of the input strain amplitude) in the range of small deformations for the GelMA hydrogels. Moreover, increasing the polymer content leads to increase the magnitude of both
and $G''$, and shifts the yield point to lower strain amplitude from $\gamma_0 = 100\%$ for 10\% (w/v) GelMA hydrogel to about $\gamma_0 = 70\%$ for 20\% (w/v) GelMA hydrogel (see the black dotted circles in Figure 6-3). The yield stress of the hydrogels (Figure S6 of Appendix D) is recorded at the highest point of the stress-strain amplitude curve, and further increase in the shear stress results in rupture of the hydrogels. Thus, yield stress is an essential parameter representing the mechanical strength of the hydrogels. The higher yield stress, $G'$, and $G''$ of 20\% (w/v) GelMA hydrogel compared to its counterparts can be attributed to the existence of higher number of cross-linking sites and polymer chains contributing to the network structure. Figures S7 and S8 of Appendix D show the yield stress of 10\% (w/v) GelMA hydrogel under extensional and rotational deformations, respectively.

Figure 6-3: Oscillatory amplitude sweep response of gelatin-based hydrogels for strain amplitudes of $\gamma_0=0.1$-100\% at an angular frequency of $\omega = 1$rad/s using parallel-plate geometry at room temperature, (a) 10\% (w/v) GelMA hydrogel, (b) 15\% (w/v) GelMA hydrogel, and (c) 20\% (w/v) GelMA hydrogel. Data points indicated by arrows were used in Figure 6-4 to obtain the Lissajous-Bowditch loops. The insets show magnified $G'$ response for strain amplitudes of 10.0-100.0\%. Black dotted circles indicate yield strain. Red dotted circles indicate the onset of inter-cycle strain-stiffening behavior.

The insets in Figure 6-3 show magnified $G'$ axis for the strain amplitudes of 10.0-100.0\%. It is obvious that the critical strain amplitude (i.e., occurrence of inter-cycle nonlinearity, onset of departure of $G'$ from plateau moduli) decreases as a result of increasing the polymer content (see the red circles in the insets of Figure 6-3). Moreover, $G'$ follows an increasing trend once it exceeds the linear viscoelastic limit. Shah et al. 25 reported similar ramping trend in storage modulus of the fibrin gels in nonlinear region. Hyun et al. 26 defined four typical nonlinear behavior streams based on combined experimental and simulation analysis to classify the
complex fluids. Type I stream (strain-thinning) is a commonly observed behavior in polymer melts and solutions, that occurs when both $G'$ and $G''$ decrease in the nonlinear region as a result of the alignment of network segments with the flow field. For type II stream (strain-hardening), both $G'$ and $G''$ increase; and for type III stream (weak strain overshoot), $G'$ decreases while $G''$ first increases and then decreases. Finally, for type IV stream (strong strain overshoot), $G'$ and $G''$ initially increase followed by both decreasing. The rise in $G''$ combined with an increase in $G'$ prior to the yield for GelMA hydrogels represents type II behavior (inter-cycle strain-hardening behavior). The inter-cycle strain-stiffening behavior is characteristic of many biopolymer networks 27.

Inter-cycle strain-hardening behavior for polymer networks is governed by the following mechanisms: deformation-induced increase in the number of elastically active chains, which leads to a more compact network 28-30, and nonlinear high tension along the chains that are stretched into non-Gaussian regime 31-33. Results from three sets of experiments can be used to discriminate the governing mechanism of strain-hardening: investigating the variation (1) in relaxation time during strain-hardening, (2) phase angle ($\delta$), and (3) degree of strain-hardening.

Evaluating the behavior of the phase angle ($\delta$) (comparison of stored energy to dissipated energy) during strain-hardening can provide valuable information about the origin of strain-hardening nonlinearity. In this regard, the phase angle decreases by increasing the deformation for strain-hardening induced by the increase in the number of elastically active segments 34. Also, the phase angle increases as a result of a strain-hardening induced because of non-Gaussian stretching of the polymer chains. Figure S9 of supporting information (Appendix D) shows $\delta$ for GelMA hydrogels during strain sweep experiments. The increasing trend in $\delta$ as strain $\gamma_0$ exceeds the limit of viscoelastic linearity verifies that inter-cycle strain-hardening is resulting from non-Gaussian stretching of polymer segments among chemical cross-links.
As previously mentioned, another method to determine the mechanism governing the strain-hardening behavior is to compare the degree of strain-hardening of the storage modulus and loss modulus, defined as:

\[
\frac{G'_{\text{max}}}{G'_{\text{lin}}}, \frac{G''_{\text{max}}}{G''_{\text{lin}}} = \frac{\tan\delta_{\text{lin}}}{\tan\delta_{\text{max}}} \quad \text{eq. 6 - 1}
\]

where \(\delta_{\text{lin}}\) and \(\delta_{\text{max}}\) are the phase angle in linear regime and at maximum strain, respectively. Similarly, \(G'_{\text{lin}}\) and \(G''_{\text{lin}}\) are the storage and loss moduli in linear regime and \(G'_{\text{max}}\) and \(G''_{\text{max}}\) are the storage and loss moduli at maximum strain, respectively. If the strain-hardening results from the increase in the number of elastically active chains, the value of \(\frac{G'_{\text{max}}}{G'_{\text{lin}}}\) would be greater than \(\frac{G''_{\text{max}}}{G''_{\text{lin}}}\). However, if the strain-hardening is because of non-Gaussian stretching of the polymer segments, the value of \(\frac{G'_{\text{max}}}{G'_{\text{lin}}}\) would be smaller than \(\frac{G''_{\text{max}}}{G''_{\text{lin}}}\). Figure S10 of Appendix D indicates the degree of strain-hardening. The smaller value of \(\frac{G'_{\text{max}}}{G'_{\text{lin}}}\) with respect to \(\frac{G''_{\text{max}}}{G''_{\text{lin}}}\) reveals that the occurrence of strain-hardening behavior in covalently cross-linked GelMA hydrogels mainly stems from non-Gaussian stretching of the polymer, which is consistent with the results obtained based on the phase angle behavior discussed above. It is worthwhile mentioning that Kurniawan et al. \(^{35}\) demonstrated that the strain-stiffening behavior of self-assembled type-I collagen mainly stems from increase in the number of elastically active chains. However, for chemically cross-linked GelMA based on the results of the current work, this behavior mainly originates from non-Gaussian stretching. Based on the results of the frequency sweep tests in Figure S4 of Appendix D, it is not possible to find the origin of strain-hardening behavior based on the relaxation time given the data that the crossover frequency is not within the probed frequency window.

\(G'\) and \(G''\) are strictly defined only in the linear viscoelastic framework, and they lose the rigorous mathematical background in the nonlinear framework. As mentioned in Background section of Supporting Information (Appendix D), this is because of the presence of the higher
harmonics in output shear stress response. Thus, no longer $G'$ and $G''$ have physical meaning in the nonlinear regime and they exclusively deliver qualitative inter-cycle interpretation (e.g., inter-cycle strain-hardening behavior). We further adopted the stress decomposition method to provide a better meaningful physical explanation of the viscoelastic nonlinearity. The inter-cycle nonlinearity and intra-cycle nonlinearity are discussed below based on qualitative Lissajous–Bowditch plots (simplified as Lissajous plots) and quantitative nonlinear parameters (introduced in Background section of Supporting Information, Appendix D).

6.3.4 Lissajous–Bowditch plots.

With the aid of Lissajous curves, one can immediately find the type of intra-cycle nonlinear response of materials to an oscillatory deformation. The trajectory in linear framework is elliptic for a viscoelastic material, approaching the limiting case of a straight line for a Hookean elastic solid (the slope represents storage, elastic, modulus) and an ellipse with the axes aligned with the coordinate axes for a Newtonian fluid. Any distortion in the shape of Lissajous loops reveals the emergence and contribution of the higher harmonics in output shear stress waveform. Additionally, the area of Lissajous plots in the elastic projection is equal to the energy dissipated per unit volume in one cycle.

Figure 6-4 shows the 3-D Lissajous plots and their projections on viscous plane (output intra-cycle shear stress $\tau_{\text{raw}}$ vs. intra-cycle strain rate $(d\gamma/dt)_{\text{raw}}$) and elastic plane (output intra-cycle shear stress $\tau_{\text{raw}}$ vs. intra-cycle strain $\gamma_{\text{raw}}$) for GelMA hydrogels at strain amplitudes of $\gamma_0 = 10, 26, 50, \text{ and } 70\%$. In linear framework, i.e., $\gamma_0 < 50\%$, the Lissajous loops are practically a straight line in elastic projection conjugated with a wide ellipse shape in viscous projection. This demonstrates that the responses are dominated by the elastic response. This agrees with previous results in Figures 6-3 and S3 of Appendix D which showed that $G' >> G''$. However, the response of the GelMA hydrogels to a deformation greater than 50% is presented by a distorted ellipse-like shape in elastic projection, and the area of the Lissajous loops (i.e., the
dissipated energy) increases proportional to the increase of input strain amplitude. This indicates activation of the dissipative (or viscous) character of the hydrogel at large deformations.

It is worth noting that the total shear stress in each cycle increases on account of the increase in the polymer concentration (counter clockwise rotation of elastic Lissajous loops in Figures 6-4 (g) and (h)). Figure S11 of Appendix D also shows the maximum shear stress in one cycle of oscillation at strain amplitude of 70% for samples containing different GelMA concentrations. This reveals a higher resistance of the hydrogels to the imposed deformation by increase in the GelMA concentration, which can be interpreted as a more rigid and stronger network due to higher number of cross-links and polymer chains, which act as load bearing elements.
Figure 6-4: 3-D Lissajous-Bowditch curves for different concentrations of the polymer in GelMA hydrogel at strain amplitudes of $\gamma_0 = 10, 26, 50,$ and 70% are shown in first row. (a) elastic and (b) viscous Lissajous-Bowditch curves for 10% (w/v) GelMA hydrogel; (c) elastic and (d) viscous Lissajous-Bowditch curves for 15% (w/v) GelMA hydrogel; (e) elastic and (f) viscous Lissajous-Bowditch curves for 20% (w/v) GelMA hydrogel. (g) and (h) elastic and (i) and (j) viscous Lissajous-Bowditch curves for 10% (w/v) GelMA hydrogel (black line), 15% (w/v) GelMA hydrogel (gray line), and 20% (w/v) GelMA hydrogel (light blue line) at strain amplitude of 10% (linear regime) and strain amplitude of 70% (nonlinear regime).

The Lissajous curves become distorted upon increasing the imposed strain amplitude toward strain amplitude of the yield stress. Figures 6-4 (g)-(j) compares the Lissajous plots of the hydrogels in linear (strain amplitude of 10%) and nonlinear (strain amplitude of 70%) viscoelastic regimes with better resolution. The upward convex curves in positive domain of...
strains in elastic projection can be interpreted as intra-cycle strain-stiffening nonlinear viscoelastic behavior. Kurniawan et al. 35 have reported the same intra-cycle nonlinear response for self-assembled collagen. The structure of the cured GelMA hydrogel can be described as a network of the polymer chains chemically cross-linked by covalent bonds. A segment is defined as a part of a macromolecular chain or a microstructure that joins two successive junctions. Correspondingly, the junctions (crosslinking point) are defined as the points where the polymer chains are connected to each other via a covalent bond. In most of the network models, junctions are lost and created during the flow. Hence, the network consists of junctions with a distribution of ages. For example, Narita et al. 36 considered cross-linking sites as “stickers”, which associate one chain to another by the interactions having association and dissociation time constants. In contrast to many families of network models that determined the distribution of network junctions by their creation and loss rates 37, the number of chemical junctions is considered constant in our DC hydrogel. Meanwhile, the number of physical cross-links of the GelMA could have changed. Thus, the elastic intra-cycle nonlinearity mainly stems from finite extensibility of the polymer, in which the polymer segments (between the junctions) are stretched beyond the Gaussian range 31. This behavior will be further discussed based on nonlinear parameter in the next section.

In a recent model 38 proposed for a strain-stiffening polymer network, the stretched polymer strands (elastic elements) are considered to obey a nonlinear force-extension law in large deformations. Therefore, we considered that the polymer segments between the junctions in GelMA hydrogels act as a Hookean spring in small amplitude regime, while they follow a nonlinear force-extension law in large deformations (non-Gaussian stretching), leading to an intra-cycle strain-stiffening behavior. Determination of the type of viscous intra-cycle nonlinearity based on Lissajous plots is challenging, which brings us to the next section. Next,
we study the intra-cycle nonlinearity with a quantitative approach using nonlinear viscoelastic parameters.

6.3.5 Nonlinear intra-cycle viscoelastic parameters.

The detailed explanation of intra-cycle parameters can be found in Background section of Supporting Information, Appendix D. Table S1 and Table S2 summarize intra-cycle parameters and provide a guideline for recognizing the type of nonlinearity based on the defined parameters. Figure 6-5 shows the intra-cycle viscoelastic parameters obtained under oscillatory flow for hydrogels. \( \eta'_M \) and \( \eta'_L \) are roughly constant (Figures 6-5 (a) and (b)) and \( T \) index is close to zero (Figures 6-5 (g) and (h)) up to strain amplitude of \( \gamma_0 = 10\% \) for 10\% (w/v) and 15\% (w/v) GelMA hydrogels. These results can be interpreted as these samples having no viscous inter- and intra-cycle nonlinearity up to strain amplitude of 10\% (in line with Figure 6-3). However, it is apparent that \( \eta'_M \) and \( \eta'_L \) of the 20\% (w/v) GelMA hydrogel are not constant even in small strain amplitude region (\( \gamma_0 < 10\% \)). Thus, it could be concluded that the onset of viscous inter-cycle nonlinearity is sensitive to polymer content and decreases as the GelMA concentration increases. The overall increasing trend of \( \eta'_M \) and \( \eta'_L \) (in all probed strain amplitudes for 20\% (w/v) GelMA hydrogel and in strain amplitudes larger than 10\% for 10\% (w/v) and 15\% (w/v) GelMA hydrogels) indicates that the inter-cycle viscous nonlinearity of gelatin-based hydrogels is shear-thickening behavior.
Figure 6-5: Intra-cycle nonlinear measures; (a), (b), and (c) are local dynamic viscosities: minimum strain rate viscosity $\eta_M$ and large strain rate viscosity $\eta_L$; (d), (e), and (f) are local elastic measures: minimum strain modulus $G_M$ and large strain modulus $G_L$; (g), (h), and (i) intra-cycle viscoelastic parameters: strain-stiffening ratio ($S$) and shear-thickening ratio ($T$). Data were obtained at angular frequency of $\omega = 1\text{rad/s}$ using parallel-plate geometry at room temperature.

A similar conclusion can be obtained for the onset of viscous intra-cycle viscoelastic nonlinearity based on the behavior of $T$ index. As shown in Figures 6-5 (g), (h), and (i), $T$ index (pink filled triangles) has positive values at lower strain amplitudes when we increase the polymer content in the hydrogel, demonstrating an intra-cycle shear-thickening behavior. However, at sufficiently large strain amplitudes, the hydrogels behave differently and $T$ index becomes negative, and the nonlinear viscoelastic behavior has switched from intra-cycle shear-thickening to intra-cycle shear-thinning response. The shear-thinning nonlinearity is a typical nonlinear behavior of polymeric materials exposed to large deformations due to chain slippage. Shear-thickening behavior of the GelMA hydrogels can be explained by coexistence of chemical and physical cross-links in these hydrogels. This dual-mode cross-linking nature of
GelMA hydrogels could be activated when the polymer chains are not stretched (see Scheme 6-2). Van Den Bulcke et al. 39 studied the structural and rheological behavior of methacrylamide gelatin hydrogels, which contained both physical and chemical cross-links. Scheme 2 of their work shows the coexistence of chemical and physical cross-links in gelatin-based hydrogels, and it was shown that physical crosslinks are formed due to the interference of gelatin chains with helix formation. They mentioned that these cross-links have physical origin (e.g., hydrogen bonding). Benton et al. 40 also mentioned the coexistence of both physical and chemical cross-links in GelMA hydrogels, and therefore, these hydrogels have the advantage of more easily tunable mechanical properties.

Scheme 6-2: Nonlinear local dynamic viscosities measurement at corresponding position of the oscillating plate in one cycle of oscillation and the state of hydrogel structure and DC cross-links nature of GelMA hydrogels.

The above discussion rationalizes the occurrence of the intra-cycle shear-thickening behavior at intermediate deformations. In this regard, as the oscillating rheometer’s plate displaces from zero deformation to the largest deformation in each cycle, polymer chains are stretched by the applied shear stress. Therefore, the number and size of the helices (chain
interference) decrease, and consequently, the physical cross-links are destroyed, and a weaker hydrogel is expected (see Scheme 6-2, right side). However, when the rheometer’s plate returns to the starting point, i.e., zero deformation, the chains can reform the helices and the physical cross-links are formed again. Hence, $\eta_L'$, measured at starting point, is greater than $\eta_M'$, measured at turning point. This behavior is sensitive to polymer concentration and occurs at a smaller deformation as the polymer content increases. Moreover, shear-induced structure formation has been widely reported as another mechanism for shear-thickening behavior for polymer hydrogels 41-43. When the upper plate returns back to zero deformation, hydrogels experience the highest shear rate, which may cause shear-induced gelation. Hence, this increase in $T$ index occurs either by new shear-induced network junctions or engagement of previously elastically inactive cross-link sites once a certain local strain is reached.

However, the occurrence of intra-cycle shear-thinning behavior (negative $T$) at larger strain amplitudes can be attributed to yielding of physical bonds and slippage of the polymer chains due to extremely high shear rates at starting position (zero deformation). Additionally, at larger strain amplitudes, since angular frequency is constant, the rheometer’s plate passes the starting position in a shorter time. Thus, the polymer chains would not have enough time to relax and reform the physical cross-links, i.e., the helical structures.

We postulated that, viscous nonlinearity at moderate strains (shear-thickening) originates from physical cross-links. Figure S12 of Appendix D proves this hypothesis, which shows the same viscous nonlinear behavior for an uncured hydrogel containing 10% (w/v) GelMA. In a future publication, we will compare the nonlinear viscoelastic behavior of the cured and uncured GelMA hydrogels to delineate the contributions of physical and chemical cross-links to rheological parameter values in nonlinear viscoelastic behavior.

In Figure 6-5 (d), (e), and (f), nonlinear viscoelastic parameters $G_M'$ and $G_L'$ were plotted against strain amplitude for GelMA hydrogels. The values of $G_M'$ and $G_L'$ are equal and constant
in small deformation region, which results in a roughly zero $S$ index, indicating no intra- and inter-cycle elastic nonlinearity in the samples. However, exceeding the linear viscoelastic limit, the change in the value of the $G'_M$ and $G'_L$ and the divergence of these moduli from each other, mark the emergence of both inter- and intra-cycle elastic nonlinearity. In this regard, in the nonlinear range, $G'_L$ is shown to be larger than $G'_M$, resulting in a positive $S$ index that can be interpreted as intra-cycle strain-stiffening response. As mentioned earlier, this behavior originates from stretching of the polymer segments between two successive junctions. Polymer segments would obey a nonlinear force-extension law under large deformation. Hence, as the polymer chains are stretched in large deformations, they would act stiffer. Therefore, more shear force is required for further increase in deformation from one cycle to another. This leads to inter-cycle strain-stiffening response. The same phenomenon happens in each cycle. As the strain starts increasing in each single cycle by displacing the upper plate of the rheometer from $\gamma_0 = 0$ towards $\gamma_0$, the chains become more and more stretched. Therefore, for cycles with sufficiently large displacement ($\gamma_0 > 10\%$), the polymer strands follow a nonlinear force-extension law as the displacement starts increasing from $\gamma = 0$ to $\gamma = \gamma_0$ and, thus, the hydrogels experience intra-cycle strain-stiffening nonlinearity in each cycle.

We conclude that hydrogels obey a nonlinear force-extension law in large deformations leading to intra- and inter-cycle strain-stiffening elastic nonlinearity. In addition, the viscous intra-cycle nonlinearity occurs because of the physical cross-links in chemically cured GelMA hydrogels. We found that nonlinear parameters are extremely sensitive to the microstructure of the hydrogels, and that the nonlinear viscoelastic properties under oscillatory shear flow are very useful for hydrogel systems characterization.

6.4 Conclusions

In this work, nonlinear viscoelastic behavior of covalently cross-linked hydrogels was evaluated under multiple strain amplitudes using oscillatory shear flow. Gelatin methacryloyl
(GelMA) hydrogel was prepared at different GelMA concentrations, and its structure was characterized using imaging techniques. We also investigated the linear viscoelastic properties obtained under small amplitude oscillatory shear (SAOS) flow. The results of SEM micrographs and linear viscoelasticity confirmed formation of GelMA network. The samples were then subjected to oscillatory flow at multiple strain amplitudes. To achieve this, the hydrogels were attached to the rheometer plates using a treated glass slide and double-sided tape to eliminate wall-slip and thus diminish any error arising from wall-slip. Significant difference in rheological response of the attached and unattached hydrogels were observed, proving the significant error due to wall-slip in rheometry of the hydrogels.

Intra-cycle viscoelastic behavior of the hydrogels was interpreted both qualitatively and quantitatively. The results showed that all samples demonstrate a strong nonlinear viscoelasticity, including inter-cycle strain-stiffening (increase in $G_M'$ and $G_L'$), intra-cycle strain-stiffening (positive strain-stiffening ratio ($S$)), inter-cycle shear-thickening (increase in $\eta_M'$ and $\eta_L'$), and intra-cycle shear-thickening (positive shear-thickening ratio ($T$)) at intermediate strains followed by an intra-cycle shear-thinning (negative shear-thickening ratio ($T$)) behavior at sufficiently large deformations. Moreover, it was shown that the onset of the viscous nonlinearity is sensitive to the polymer content in the hydrogel, and that the viscoelastic behavior can be tuned by changing the polymer content.

The results of the present work reveal new aspects of the chemically cured gelatin-based hydrogels and provide valuable information regarding the network structure of the hydrogels, which are not necessarily accessible via rheological parameters obtained within the linear viscoelastic framework. The correlation between the microstructure and viscoelastic properties under large deformations provides further guidance for fabrication of high-performance hydrogels with precisely controllable microstructures and mechanical behaviors.
6.5 Supplementary material

Figures S1-S15, and Table S1 and S2 (as mentioned in the main text).

6.6 References


Chapter 7 - Outstanding Interfacial Viscoelasticity of Graphene Oxide at Water/Air and Water/Oil interfaces: A Comparative Study

Presentation of Article:

In this work, we investigated the effect of incorporation of graphene oxide (GO) nanosheets on interfacial viscoelasticity of water/air and water/oil interfaces. Due to the dual nature of GO nanosheets, i.e., hydrophobicity and hydrophilicity, it was shown that nanosheets, even at extremely low concentrations, are very effective in film formation at the interfaces. For instance, an interfacial elastic modulus ($G_e'$) as high as 1000 mN/m at water-(0.04 vol.%GO)/oil interface was observed. Moreover, it should be mentioned that the interfacial viscoelastic properties in the presence of GO nanosheets are far greater at water/oil interface compared to water/air interface. Moreover, it was observed that the type of inter-cycle nonlinear viscoelasticity changes either by changing the top phase (oil and air) or by increasing the content of the nanosheets. In this regards, the inter-cycle nonlinearity switches from strain induced softening behavior to weak strain overshoot by changing air with oil.

Authors’ contributions: I organized and wrote the paper. I conducted the rheological measurements. Dr. Sharif helped with synthesizing nanosheets. Mr. Kannan helped with running the interfacial tension measurements. Prof. Sundararaj and Prof. Fuller supervised the whole work.
Outstanding Interfacial Viscoelasticity of Graphene Oxide at Water/Air and Water/Oil interfaces: A Comparative Study

Milad Kamkar, a&b Farbod Sharif, b Aadithya Kannan, a Gerald G. Fuller, a Uttandaraman Sundararaj *b

a Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr NW, Calgary, Alberta T2N 1N4 Canada
b Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025, USA
*Corresponding Authors: E-mail: u.sundararaj@ucalgary.ca (Uttandaraman Sundararaj)

Graphical abstract:

7.1 Abstract.

Nanoparticle-stabilized emulsification of oil in water has drawn great attention from various industries (e.g., cosmetic, food industry, and enhanced oil recovery). Due to the dual nature of graphene oxide (GO) nanosheet, i.e., hydrophobicity and hydrophilicity, it is very effective in the stabilization of water/oil emulsions. However, with respect to the water-GO/oil interface, the interfacial rheological properties remain largely unexplored. In this work we provide a systematic study to elucidate the performance of GO (at different concentrations) at water/oil interfaces utilizing interfacial rheological techniques. We also compare the interfacial viscoelastic properties of water-GO/oil and water-GO/air. The results demonstrate the excellent ability of GO nanosheets, even at extremely low concentration as 0.04vol.%, in forming an elastic-like film (interfacial elastic modulus ($G'_s$) as high as 1000mN/m) at water/oil interface. Moreover, the viscoelastic properties at oil interfaces are by far greater than those associated with air interfaces at all GO concentrations.
7.2 Introduction.

Graphene oxide (GO) is the product of chemical exfoliation of graphite. GO has been known to disperse well in water. GO nanosheets form 2D crystalline surfaces with large specific surface areas. These are conjugated with one atomic layer thick structure of GO nanosheets, making GO an outstanding candidate among the other carbonaceous nanomaterials for the design of materials with a wide range of applications (e.g., electrical, mechanical, etc.). The mentioned physical features of graphene nanosheets, combined with their amphiphilicity (originating from carbon ring basal plane) and hydrophilicity nature (stemming from surface functional groups e.g., hydroxyl, carboxylic and epoxy groups), make them a versatile nanomaterial for nanoparticle-stabilized water/oil emulsions. For instance, Sun et al. have shown the diffusion of GO nanosheets to the oil/water interface and the formation a film parallel to the interface. This is due to the flexible nature of GO nanosheets, enabling them to be anchored at the interface.

Kim et al. investigated the activity of GO nanosheets at air-liquid, liquid-liquid, and liquid-solid interfaces. The authors demonstrated that despite the stable dispersion of GO nanosheets in water, GO can adsorb onto interfaces and lower interfacial tension. Imperiali et al. have studied the GO film at water/air interfaces employing compression/expansion experiments in a Langmuir trough and shear rheometry (creep and recovery). However, to the best of our knowledge, there is no work in literature systematically studying and comparing the viscoelastic properties of GO film at water/oil or water/air interfaces. Moreover, the mechanical properties of the interfacial assemblies has been considered as a key factor in the stability of emulsions stabilized by GO sheets. For these reasons, we aimed to provide fundamental insights into the interfacial viscoelastic response of GO film at water/oil and water/air interfaces utilizing oscillatory interfacial shear flow in both linear and nonlinear viscoelastic regions. These results are combined with interfacial tension measurements.
7.3 Materials and methods.

7.3.1 Oil phase.
Silicone oil (5 cSt, Clearco #63148-62-9) was used as the oil phase in the experiments.

7.3.2 Graphene oxide synthesize.
GO was synthesized from natural graphite flake. Briefly, graphite powder (Asbury Carbon, Natural flake) and sodium nitrate (2:1 ratio) (Sigma Aldrich, ReagentPlus®, ≥ 99%) were mixed with concentrated sulfuric acid in an ice bath. Afterwards, potassium permanganate was added to the mixture (3:1, KMnO4: graphite) (Anachemia, Reagent Grade, 99%) under intense stirring and the temperature was maintained lower than 20°C. Then the mixture was vigorously stirred at 35°C until a brownish pasty mixture formed. The graphite mixture was gradually diluted with deionized water in an ice bath to keep the temperature lower than 50°C. A solution of deionized water containing hydrogen peroxide (Sigma Aldrich, Reagent Grade, 30%) was then mixed with the suspension and stirred for another 2h. After separation via centrifugation, the solids were washed using an aqueous solution contacting HCl to eliminate any residual ions. The graphite oxide was again rinsed with DI water. The collected graphite oxide was exfoliated in water under bath sonication. The large unexfoliated solids were separated from the GO by centrifugation at 4000rpm.

7.3.3 Interfacial tension and interfacial rheology.
Interfacial tension at water/air or water/oil interfaces has been measured using Wilhelmy plate coupled to an electrobalance (KSV Nima, Finland). The interfacial rheological tests were conducted using a DHR-3 rheometer from TA instruments equipped with a double wall-ring device with a du Noüy ring employed as the interfacial element. The detailed procedure of setup preparation is provided elsewhere. To study the interfacial viscoelasticity, time sweep tests (at $\omega = 0.5\text{rad/s}$ and strain amplitudes of $\gamma_0 = 0.1\%$) followed by frequency sweep (strain amplitude of $\gamma_0 = 0.1\%$) and strain amplitude sweep (at angular frequency of $\omega = 1.0\text{rad/s}$) tests...
were performed on all samples at ambient temperature. Duplicate measurements were made for all the samples to demonstrate reproducibility.

7.4 Results and discussion.

7.4.1 Graphene oxide characterization.

To confirm the presence of the functional groups on the surface of the GO, Raman spectroscopy measurements were carried out. The Raman Spectra of the graphene is typically characterized by the D band (ca. 1350 cm\(^{-1}\)), arising from breathing mode of the sp\(^2\) carbon atoms as a result of the defects in the graphene structure (attributed to functional groups), and G band (ca. 1580 cm\(^{-1}\)), coming from in-plane vibration of sp\(^2\) carbon atoms (originated from carbon ring of the basal plane).\(^{13}\) Strong D and G peaks can be observed in the GO Raman spectrum in Figure 7-1 (a), indicating very small crystal sizes, which is characteristic of the GO. The presence of a sharp D band suggests existence of defects such as vacancies generated during the oxidation of graphite and consequently formation of the oxygen functional group on the basal plan of the graphene oxide.

In order to identify the bonding present in synthesized graphene oxide, ATR-FTIR spectroscopy was utilized to analyze the sample. FTIR spectra were obtained in the range 4000–600 cm\(^{-1}\) using a mid-IR KBr-DTGS detector. The ATR-FTIR spectra recorded for GO, is depicted in Figure 7-1 (b). The peaks at 1210 and 1033 cm\(^{-1}\) are owing to existence of the epoxy groups (C–O and C–O–C) on the surface and periphery of the GO. The characteristics peaks at 1740 and 1620 cm\(^{-1}\) can be attributed to the stretching vibration of the carbonyl (C=O) and carboxylic groups (R–COOH) of C and O bonds, and skeletal vibration of graphitic domains, respectively.\(^{14-15}\)

The result of thermogravimetric analysis (TGA) of GO is presented in Figure 7-1 (c). GO exhibited a small mass loss below 160°C as a result of water volatilization, a substantial mass loss between 160–225°C due to decomposition of labile oxygen containing functional
groups, and another slight mass loss around 900°C attributable to elimination of the excess functional groups.16-17 As it can be seen, more than 60% of the synthesized GO is composed of the oxygen functional groups. The TGA results are in line with Raman and FTIR results. The aqueous GO dispersions (at different GO concentrations) have been used to study interfacial rheology in the next sections. Figures 7-1 (d) and (e) show the transmission electron microscopy (TEM) images of synthesized GO. It is clearly shown in TEM images that GO nanosheets are single layered materials.

![Figure 7-1](image)

**Figure 7-1:** (a) Raman spectra, (b) ATR-FTIR spectra, (c) TGA, and (d) and (e) TEM images of GO (scale bar = 200nm).

### 7.4.2 Interfacial film evolution (transient viscoelasticity).

In the first step of this work, GO structuring (film formation) at the interface has been probed by monitoring the interfacial elastic ($G_s'$) modulus, the loss ($G_s''$) modulus, and the interfacial tension of water-GO/oil and water-GO/air over time. Figures 7-2 (a) and (b) present $G_s'$ and $G_s''$ of water-GO/oil and water-GO/air interfaces with 0.1 and 0.3vol% GO nanosheets in aqueous phase (see Figure S1 of Appendix E for systems containing 0.01 and 0.2vol% GO nanosheets).

In conducting the interfacial rheometry of water-GO/air systems, the du Nouy ring was located
at the interface immediately after pouring the aqueous GO dispersion system in the double-wall cup, and for water-GO/oil, time \( t = 0 \) corresponds to the addition of oil on top of the GO aqueous systems.

Figure 7-2: (a) and (b) evolution of interfacial elastic \( G'_s \) and loss \( G''_s \) moduli of aqueous dispersion of GO at air and oil interfaces at 0.1 and 0.3vol\% of GO. Time sweep test has been conducted instantly after loading the samples at strain amplitude of \( \gamma_0 = 0.1\% \) and angular frequency of \( \omega = 0.5\text{rad/s} \). (c) interfacial tension of aqueous suspension of GO at air and oil interfaces at 0.1 and 0.3vol\% of GO. The rheological tests have been conducted at ambient temperature using a du Noüy interfacial geometry. We used standard deviation for error bars on each side.

As can be seen in Figure 7-2, the evolution of the GO film at the interface is relatively rapid as \( G'_s \) grows within the first few seconds of the experiment until a quiescent cohesive interfacial film is formed. However, comparing the viscoelastic moduli at water-GO/air and water-GO/oil interfaces reveals that the kinetic of GO structuring at oil interface is dramatically faster than air interface.

The GO films at oil interfaces show a viscous-like behavior in initial stages \( (G'_s < G''_s) \). However, a rapid viscoelastic viscous-to-elastic transition occurs \( (G'_s > G''_s) \) at approximately 30s as the \( G'_s \) at oil interface develops so quickly. Afterwards, water-GO/oil interfaces possess a strong elastic-like behavior \( (G'_s \) is comparatively greater than \( G''_s) \) at all GO concentrations
(even at 0.04vol%). However, water-GO/air interfaces feature a weak viscoelastic response and behave as a low-viscosity fluid interface at low GO loadings (see Figures 7-2(a) and S1(a) of Appendix E). This interpretation is deduced from the fact that $G'_s$, which is approximately 47mN/m, is initially an order of magnitude greater than $G''_s$, which is 4mN/m, for water-GO(0.1vol%)/air and the liquid-to-solid transition takes place at longer times. For instance, the interfacial elastic character of water-GO(0.1vol%)/air supersedes the viscous nature after 250s (see the insets in Figures 7-2(a)).

Comparing the $G'_s$ at air and oil interfaces demonstrates that $G'_s$ at water-GO/air is almost constant over time while the $G'_s$ at water-GO/oil follows a different pattern and it drops rapidly in the initial stages of the experiment followed by a moderate decay at longer times. The simultaneous dramatic increase in $G''_s$ and decrease in $G''_s$, which result in a considerable decrease in the value of the damping factor ($\tan \delta < 1$), confirms that domination of the solid-like behavior of the GO film at water/oil interface becomes more pronounced as time passes.

These results verify that the GO film at oil interfaces is more structured than air interfaces. To provide further insight into the GO network structures at different interfaces, the interfacial tension of water-GO/oil and water-GO/air at various GO concentrations as a function of time is given in Figure 7-2 (c). The interfacial tensions of water/oil and water/air interfaces (see green lines in Figure 7-2 (c)) were found to be 32 and 72mN/m, respectively. As can be seen in Figure 7-2 (c), the dynamic interfacial tension of water-GO(0.1vol.%)/air is close to water/air (71mN/m) and it decreases to 67mN/m over time, indication of formation of interfacial active GO film at the water surface. Moreover, as the GO loading increase to 0.3vol.%, the initial value of surface tension at water-GO/air interface decreases to 53mN/m and decays to 50mN/m as time passes. Furthermore, by oil addition, the initial value of interfacial tension decreases dramatically to 25 and 15mN/m for water-GO/oil containing 0.1 and 0.3vol.% GO, respectively. The results of interfacial tension are in line with escalation of
interfacial viscoelastic properties by increasing the GO loading, aging the systems, or replacing air and oil, as shown in Figures 7-2 (a) and (b).

Taken together, GO nanosheets exhibit noticeably greater interfacial activity at the oil interface compared to air interface as confirmed by interfacial viscoelasticity and interfacial tension. Based on the data provided in Figure 7-1, 60% of the synthesized GO is composed of the oxygen containing groups, and the remaining is nonpolar carbonaceous basal plane. Thus, the superior interfacial properties of GO suspension at oil interface can be correlated to interaction of carbon ring basal plane of GO with nonpolar groups of oil. The more chemical heterogeneity at the interface upon addition of oil, the more irregular wetting of the perimeter and planar surface of GO, which leads to higher liquid menisci around the nanosheets, causing stronger lateral capillary forces.

7.4.3 Frequency sweep and strain sweep.

In this section, we aimed to provide further information on interfacial viscoelasticity of water-GO/oil and water-GO/air by studying the interfacial elastic ($G'_s$) modulus and loss ($G''_s$) at multiples strain amplitudes and angular frequencies. To achieve this, linear rheological test (frequency sweep) followed by destructive nonlinear rheological test (strain amplitude sweep) have been performed on the samples after GO film formation at the interface, i.e., after linear time sweep tests. Frequency sweep test has been conducted at angular frequencies ranging from $\omega = 0.1$ to $16 \text{rad/s}$ at strain amplitude of $\gamma_0 = 0.1$ and strain amplitude sweep test probed the strain amplitude window of $\gamma_0 = 0.01$ to $200\%$ at angular frequency of $\omega = 1.0 \text{rad/s}$.

Figure S2 of Appendix E shows the interfacial linear viscoelastic parameters (elastic ($G'_s$) modulus, loss ($G''_s$) modulus, and complex viscosity $|\eta^*|$). As can be seen in Figure S2, all the interfacial viscoelastic parameters are significantly greater at oil interface compare to air interface and $G'_s$ and $|\eta^*|$ of water-GO/oil at extremely low loading of 0.04vol% are, respectively, as high as 1000mN/m and 16000mPa.s.m. Considering the extremely low
concentration of GO, these values are among the highest interfacial viscoelastic values reported in literature.

Figure 7-3 shows the strain amplitude dependency of $G'_s$ and $G''_s$ of water-GO/air and water-GO/oil containing 0.1 and 0.3 vol% GO nanosheets (see Figure S3 of Appendix E for 0.04 and 0.2 vol%). In line with time sweep and frequency tests, water-GO/oil interface possesses higher elasticity at all GO loadings in linear region. More importantly, the strain amplitude sweep test offers additional information regarding interfacial viscoelastic behavior and sheds light upon the type of nonlinear viscoelasticity of water-GO/air and water-GO/oil. Comparison of Figures 7-3 (a) and (b) with Figures 7-3 (c) and (d) reveals a clear difference in inter-cycle nonlinear interfacial viscoelastic response of the water-GO/air and water-GO/oil as the strain amplitude increases and exceeds the limit of linearity. As can been in Figures S3 (c) of Appendix E, S3 (d) of Appendix E, and 7-3 (c), the interfacial nonlinearity of water-GO/air follows strain thinning behavior. The origin of strain thinning is believed to be similar to that of shear thinning (collapse of nanosheets interfacial structure and orientation or alignment of microstructures parallel to flow direction leading to decrease in intermolecular interactions and causing the local drag reduction).

However, the type of inter-cycle interfacial viscoelastic nonlinearity at oil interfaces to produce a weak strain overshoot for all GO concentrations even as low as 0.04 vol%. It is worth mentioning a weak overshoot was also captured at air interface at high concentration of GO (see the inset in Figure 7-3 (d)). Formation of complex structures (GO-GO and GO-oil interactions), which can tolerate intermediate deformations up to a certain strain, where loss moduli grows, is thought to be the origin of weak overshoot nonlinear behavior. At sufficiently large strain amplitude these structures are destroyed leading to decrease in $G''_s$.

Hence, not only do GO nanosheets have higher linear interfacial viscoelasticity at oil interface compared to air, but also the inter-cycle nonlinear viscoelastic behavior at the
interface of water-GO/air switches, from strain thinning to weak strain overshoot for water-GO/oil. In brief, there are significant differences in both linear and nonlinear viscoelastic response at the interfaces of water-GO/air and water-GO/oil.

Figure 7-3: interfacial elastic ($G'$) and loss ($G''$) moduli of aqueous suspension of GO at (a) and (b) oil and (c) and (d) air interfaces at 0.1 and 0.3vol% of GO as a function of strain amplitude at an angular frequency of $\omega = 1.0\text{rad/s}$. The rheological tests have been conducted at ambient temperature using a du Noüy interfacial geometry.

7.5 Conclusions

This work demonstrates the outstanding interfacial structuring of graphene oxide (GO) nanosheets at oil and air interfaces employing oscillatory interfacial rheological techniques (time sweep, frequency sweep, and strain amplitude sweep). To do this, aqueous dispersions of nanosheets at various GO concentrations have been prepared by synthesizing GO in aqueous media. It was shown that the interfacial activity of the nanosheets at oil interface is noticeably higher than air interface. A high interfacial storage modulus (1000mN/m) was observed at an extremely low GO loading of 0.04vol.% at oil interface, while the storage modulus was approximately 7mN/m at air interface for the same GO concentration. Moreover, the type of interfacial inter-cycle nonlinear viscoelasticity changes by replacing the air with oil. The
rheological results were verified by interfacial tension measurements. The results of these work pave the way for the development of new class nanoparticle-stabilized emulsification of oil in water and opens up opportunities to design new functional GO-based materials, e.g., bijels.

7.6 References


Chapter 8 - Conclusions and future works.

8.1 Conclusions

New rheometers with high torque resolution enable measurement of intra-cycle nonlinear viscoelastic response of complex fluids with great accuracy. The number of publications pertaining to nonlinear viscoelastic response of materials under large amplitude oscillatory shear (LAOS) flow has significantly increased in the last decade.\(^1\) However, with respect to viscoelastic nonlinearity of polymeric systems, the majority of the literature has focused on unfilled polymeric systems (e.g., dilute polymer solutions). Therefore, viscoelastic nonlinearity of polymer nanocomposites remains largely unexplored. Hence in this dissertation, we tried to improve the current state of LAOS by exploring inter- and intra-cycle nonlinear viscoelastic behavior of a wide range of complex polymeric materials, i.e., polymer nanocomposites, hybrid polymer nanocomposites, hydrogels, and interfaces, under LAOS flow.

In addition to exploring the effect of different factors (e.g., dispersion state of nanofillers, concentration of nanofillers, physical features of nanofillers, concentration of polymer in hydrogels, etc.) on nonlinearity, we also highlighted the effect of different artifacts on intra-cycle viscoelastic response of the mentioned systems. Afterwards, we provided solutions for avoiding the issues associated with these artifacts (e.g. bad data leading to wrong inferences). Hence, this dissertation addressed two important questions: 1) how can we tune the nonlinear viscoelasticity of polymeric systems by controlling different factors? and 2) how do artefacts affect the viscoelastic data associated with large and rapid deformations? The answer to the first question is explored in chapters 3-5 where we focused on LAOS behavior of CNT-based polymer nanocomposites. The main goal of these chapters is to investigate the effect of CNT microstructure on nonlinear viscoelastic response of polymer nanocomposites. Hence, the dispersion state and network structure of CNTs were manipulated employing different techniques. In our previous work,\(^2\) it was shown that synthesis temperature
considerably affects the physical structure of the CNTs, which in turn leads to different dispersion state of CNTs. In chapter 3, we were able to achieve different CNT microstructure by tuning the physical features of CNTs via synthesizing CNTs over a Fe catalyst employing vapor chemical deposition (CVD) method at different temperatures ranging from 550 to 950°C at 100°C intervals. In chapter 4, the microstructure of the CNTs in a polymeric matrix was manipulated with the aid of a secondary nanofiller with similar geometry as 1D CNTs. In chapter 5, the network structure of the nanotubes was changed by preparing nanocomposites using different mixing methods. The rheological results in these chapters were also verified by electrical measurements and imaging techniques.

To explore the nonlinear rheological behavior of a greater breadth of materials, we studied viscoelastic response of hydrogels and interfaces under large deformations in chapters 6 and 7, respectively. In chapter 6, we provided an in-depth understanding and a detailed explanation of mechanical response of the covalently cross-linked GelMA hydrogels in the nonlinear viscoelastic regime under large shear deformations. In chapter 7 of this thesis, the interfacial viscoelastic properties of water/oil were tuned by the aid of nanomaterials.

The nonlinear rheological observations in chapters 3-7 were explained using quantitative nonlinear parameters (strain-stiffening ratio ($S$) and shear-thickening ratio ($T$)) and qualitative Lissajous-Bowditch plots. Figures 8-1 through 8-4 summarize the results of the thesis. Based on the results of these chapters, it can be concluded that improvement in the network structure of a viscoelastic media:

1- Shifts the critical strain amplitude (strain at which linear-to-nonlinear transition take place) to smaller deformations, due to the higher sensitivity of a more rigid network to deformation upon any improvement in the network structure.

2- Leads to higher extent of viscous intra-cycle nonlinearity. That is, not only the onset of viscous nonlinearity shifts to smaller strain amplitudes, but also, beyond the onset, the
intra-cycle viscous nonlinearity occurs with higher rate for stronger network. This leads to a greater absolute value of viscous nonlinearity index (shear-thickening ratio \( T \)) in deep nonlinear region (see Figure 8-1). For CNT-filled systems I postulated that the higher intra-cycle nonlinearity upon enhancement of the network by improvement in quality of nanotubes dispersion is due to contribution of both individual CNT and aggregates to the viscous intra-cycle nonlinearity (i.e., disruption of CNT network structure and orientation of individual CNTs and nanotube rich domains parallel to flow direction at high shear rates associated with large deformations). For hydrogels the more pronounced viscous intra-cycle nonlinearity upon strengthening the structure is attributed to yielding of more physical bonds and slippage of more number of polymer chains due to extremely high shear rates at starting position of the upper plate of the rheometer (zero deformation).

3- In contrast to viscous intra-cycle nonlinearity, the value of the elastic intra-cycle index \( S \) at maximum deformation decreases upon improvement in nanotubes dispersion quality or enhancement in polymer network structure (see Figure 8-1). This is because the elastic nonlinearity mainly stems from the viscoelastic nature of polymer chains. That is, shear-induced stretching in polymer chains extending into the non-Gaussian regime is responsible for intra-cycle elastic nonlinearity. Hence, the value of the \( S \) index (i.e., the representative of intra-cycle elastic nonlinearity) shifts to lower values by improvement in network structure of the nanofillers. This means the chains of the polymers are less stretched in the presence of the nanofillers. This is due to the existence of nanofillers acting as load bearing zones in the polymer media via strong interactions along a huge interfacial area between the CNTs and polymer. Hence, less shear force is applied on polymer chains, and, consequently, they are less stretched.
Figure 8-1: Effect of reinforcing network structure of nanofillers in polymeric systems on intra-cycle viscoelastic parameters (strain-softening ratio \( S \) and shear-thickening ratio \( T \)). The elastic intra-cycle nonlinearity occurs mainly due to chain deformation and stretching at large strain amplitudes. Hence, improvement in network structure leads to decrease in intra-cycle elastic nonlinearity. In contrast to intra-cycle elastic nonlinearity, intra-cycle viscous nonlinearity becomes more pronounced upon strengthening the polymeric system network structures, which can be correlated to the orientation of the rigid components of the systems in the flow direction.

Based on the result of the chapter 7, the inter-cycle nonlinearity of interfaces changes from strain-softening to weak strain overshoot behavior upon reinforcing the interface.
The answers to the second question related to artifacts are summarized in Figures 8-3 and 8-4. In this dissertation, artefacts related to the effects of confinement and wall-slip phenomenon on inter- and intra-cycle viscoelastic nonlinearity were studied and the results are summarized as follows:

1- In chapter 3 of this thesis, interestingly, we observed higher storage modulus for polymer nanocomposites with poor dispersion state of nanomaterials. Additionally, inter-cycle nonlinear behavior of poorly-dispersed systems followed a multi-step yielding behavior. However, well-dispersed systems showed a smooth single-step yielding upon transition into the nonlinear regime (see Figure 8-3). Moreover, a strong intra-cycle dissipative feature accompanied by a maximum in loss modulus was observed in the medium strain amplitude region for poorly-dispersed systems. Multiple gap-size rheometry demonstrated that the mentioned behaviors (e.g., intensified solid-like behavior in low frequency region and intra-cycle dissipative feature in medium
amplitude region) of poorly-dispersed polymer nanocomposites stem from confinement
of big agglomerates of CNTs between the metal plates of the rheometer. However, the
solid-like behavior of well-dispersed systems was gap-size invariant and was correlated
to screening of the ultraslow relaxation process associated with the mesoscale structure
of the well-dispersed nanofillers.
Figure 8-3: Effect of confinement of the agglomerates of nanofillers between the plats of the rheometer on inter- and intra-cycle nonlinear behavior of polymeric nanocomposites. The confinement effect impacts both inter- and intra-cycle response. That is, the poorly-dispersed systems containing gap spanning aggregates follow a two-step inter-cycle yielding process upon exceeding the limit of the linearity. Moreover, these systems feature an intra-cycle dissipative response in medium amplitude region (positive $T$ index). Additionally, the distortion in output shear stress response and Lissajous- Bowditch plots is higher for systems containing confined structures.

2- Chapter 6 showed that the rheological response of hydrogels at large deformations is highly affiliated with wall-slip error. That is, the observed type III inter-cycle behavior (weak strain overshoot) of the hydrogels (which is the widely reported nonlinear behavior for hydrogel), switched to type II inter-cycle behavior (strain-hardening) when
the wall-slip error was eliminated. Moreover, as can be seen in Figure 8-4, the extent and location of the occurrence of both viscous and elastic intra-cycle nonlinearity over the probed strain amplitude window are significantly influenced by wall-slip phenomenon. To alleviate any error arising from wall-slip phenomenon at the interface of the metal plate of the rheometers and hydrogels at large deformations, we proposed a novel technique by chemically bonding the hydrogels to treated glass-slides which are attached to the oscillating metal plates using a double-sided tape. Using this method, we were able to capture the true inter- and intra-cycle viscoelastic response of the hydrogels at large deformations.
Figure 8-4: Effect of wall-slip phenomenon on inter- and intra-cycle nonlinear response of the polymeric hydrogels. Wall-slip phenomenon impacts both inter- and intra-cycle behavior. The inter-cycle behavior upon transition into nonlinear regime is type III (weak strain overshoot) in the presence of wall-slip. While, we observed type II inter-cycle behavior after eliminating wall-slip error. Moreover, wall-slip also affects the onset and extent of both elastic and viscous intra-cycle nonlinearity.

In summary, the results of this Ph.D. dissertation demonstrate that nonlinear viscoelastic measures are extremely sensitive to subtle changes in internal microstructures of complex materials and yield valuable information regarding the network structure of viscoelastic systems. These results are not accessible via rheological parameters obtained within the linear framework. Hence, this confirms that LAOS can be used as a powerful tool to study microstructure of complex materials and categorize them based on their nonlinear response.
8.2 Recommendations for future work

Results of this dissertation can be the foundation for proposing themes for future researcher. Several recommendations are listed below.

✔ As discussed in chapter 3, physical features of carbon nanotubes (CNTs) have a major impact on microstructure and, hence, on the nonlinear rheological behavior of the polymer nanocomposites. Surface covalent functionalization of nanofillers also dramatically affects the mesoscale structure of nanofiller network structures, which, can impact the viscoelasticity of the nanocomposites. Hence, it is suggested to study the effect surface functionalization of nanotube on nonlinear viscoelasticity of CNT-based nanocomposites. In this regard, exploring the effects of different types of functional groups, based on the continues polymer matrix (polar or nonpolar), and also the effects of different amount of functionalization on the surface of nanotubes can provide a rich source of information for tuning nonlinearity of CNT-based nanocomposites.

✔ In chapter 3, the physical features of CNTs were manipulated by synthesizing the nanotubes at different temperatures over Fe catalyst. It was found that the optimum temperature to synthesize CNTs is 650ºC. However, to investigate the effects of just length and diameter of CNTs on final electrical and rheological properties, it is suggested to synthesize CNT at 650ºC over different catalyst or at different synthesis times. This can give further insight into the mechanisms behind the relationship between physical features of nanotubes and network structure from rheological point of view.
✓ We can study the effect of doping CNTs on polymer-nanotubes interactions and the final network structure of CNTs in polymer matrices employing nonlinear rheological techniques.

✓ In this dissertation, impact of addition of 1D nanowires on network structure of 1D nanotubes was studied. It is suggested to investigate the influence of secondary nanofillers with different geometries (e.g., 2D and spherical) on CNT network formation in polymeric matrices. This will provide further and complementary information about the hybrid microstructures.

✓ We propose investigating the nonlinear rheological properties of injection molded samples versus compression molded samples. CNT aspect ratio decreases during injection molding process,\(^5\)\(^-\)\(^7\) thus, this investigation will be important due to significant impact of CNT aspect ratio on nonlinear rheological properties (CNT aspect ratio is decreased by more severe processing technique).

✓ Investigation of nonlinear viscoelastic response of polymer blend systems is another study that can be done from different point of views. For instance, the effect of morphological features of polymer blends on nonlinear rheology can provide valuable information for polymer processing industries. The morphology can be tuned by several factors (e.g., thermodynamic and kinematic factors). In this regard, the effect of processing conditions, e.g., order of addition, mixing speed, processing temperature, etc., on the resulting morphology and nonlinear viscoelasticity can provide valuable data. In the case of polymer blend nanocomposites, the morphology can be also
manipulated by nanofillers, for instance, nanofillers localization dramatically affect the morphology. Hence, nanofillers localization can dramatically affect the final rheological properties.

In chapter 6, it has been shown that the rheological response of the hydrogels is highly associated with wall-slip effect. Hence, we provided a novel method to eliminate the wall-slip effect. However, the common method to eliminate wall slip effect in the literature is using sandpaper. It is suggested to compare the efficiency of our method in reducing the wall-slip error with commonly used methods in literature like using sandpaper).

GelMA-filled nanomaterials has been widely used in tissue engineering. Hence, studying the effect of incorporation of nanomaterials on nonlinear viscoelasticity of GelMA hydrogels is of utmost importance in designing artificial tissues.

In chapter 7, it was shown that graphene oxide (GO) nanosheets are able to form a strong film at the interface of water/oil. Based on literature, mixture of GO nanosheets and aqueous polymeric solution can have synergistic effect on oil-in-water emulsification. In this regard, the rheological properties of GO nanosheets aqueous polymeric solutions at oil interface remain largely unknown. Hence, it is suggested to explore the combine effect of polymers and nanomaterials on interfacial rheology of oil/water systems.
8.3 References


Appendix A– Supplementary information for chapter 3

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

Milad Kamkar\textsuperscript{a}, Soheil Sadeghi\textsuperscript{a}, Mohammad Arjmand\textsuperscript{b}, Uttandaraman Sundararaj\textsuperscript{a,∗}
\textsuperscript{a} Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr NW, Calgary, Canada T2N 1N4
\textsuperscript{b} School of Engineering, University of British Columbia, Kelowna, BC, Canada V1V 1V7
\textsuperscript{∗}Corresponding Author: Tel: +1-403-210-6549, Email: u.sundararaj@ucalgary.ca

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}.

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 1.0wt% of carbon nanotubes synthesized at 650°C and 950°C using cone-plate (at a truncation of 47μm 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 CNT\textsubscript{950} 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 CNT\textsubscript{650}/PVDF and CNT\textsubscript{950}/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 $\tau_{raw}$ response and intra-cycle input strain waveform $\gamma_{raw}$ 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 (i)) 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 ω = 10rad/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$_{650}$ 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$_{950}$ 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$_{950}$ 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.

![Graphs showing Lissajous-Bowditch loops](image)

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 $\omega = 10\text{rad/s}$. 

200
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. 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.](image)

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

![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.](image)

Dissipated energy per unit volume. Yziquel et al.\textsuperscript{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:
\[ E_d = \int_{\text{cycle}} \tau \, dy \quad \quad \quad Eq. 1 \]

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).

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

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 rad/s. Further decrease in frequency (ω=1 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. 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 CNT950/PVDF nanocomposite.

Figure S15. Elastic (S) and viscous (T) intra-cycle nonlinearity indices as a function of strain amplitude for poorly-dispersed CNT550/PVDF, CNT850/PVDF, and CNT950/PVDF nanocomposites containing 1.0wt% of carbon nanotubes at different gap-sizes using a 25mm parallel plate geometry at strain frequency of \( \omega = 10 \text{ rad/s} \).

Loss modulus of PVDF and poorly-dispersed CNT950/PVDF.

Figure S16. Loss modulus of PVDF and poorly-dispersed CNT950/PVDF.
TEM micrographs of CNTs.


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

Table S9-1. Maximum storage modulus ($G'$) and loss modulus ($G''$) in amplitude sweep test for PVDF and PVDF/CNTs

<table>
<thead>
<tr>
<th></th>
<th>PVDF</th>
<th>CNT$_{550}$</th>
<th>CNT$_{650}$</th>
<th>CNT$_{750}$</th>
<th>CNT$_{850}$</th>
<th>CNT$_{950}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G'_\text{max}$ [kPa]</td>
<td>7</td>
<td>26</td>
<td>9.8</td>
<td>7.9</td>
<td>157</td>
<td>408</td>
</tr>
<tr>
<td>$G''\text{max}$ [kPa]</td>
<td>16.8</td>
<td>18.9</td>
<td>19</td>
<td>17.9</td>
<td>21.7</td>
<td>49.8</td>
</tr>
</tbody>
</table>

References


Appendix B – Supplementary information for chapter 4

Supplementary information for

Application of Nonlinear Rheology to Assess the Effect of Secondary Nanofiller on Network Structure of Hybrid Polymer Nanocomposites

Milad Kamkar, Ehsan Aliabadian, Ali Shayesteh Zeraati, and Uttandaraman Sundararaj*

Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr NW, Calgary, Canada T2N 1N4
*Corresponding Author: Tel: +1-403-210-6549, Email: u.sundararaj@ucalgary.ca (Uttandaraman Sundararaj)

Start-up shear

Figure S1 shows the transient start-up shear results for neat PVDF and polymer nanocomposites containing 2.0wt% CNT and different ratios of MnO₂NW.

Figure S1. Shear stress as a function of time at T=240°C and \( \dot{\gamma} = 1.0 \text{s}^{-1} \) for neat PVDF and nanocomposites.

Chebyshev coefficients

Figure S2 and S3 depict the normalized Chebyshev spectrums. Because there is no distortion in output shear stress signal within the linear framework, \( e_3 \) and \( v_3 \) approach zero and in nonlinear viscoelastic regime the value of these coefficients increase. Based on these results, the sufficiently large and positive \( e_3 \) for the elastic response can be attributed to strain-stiffening behavior and the negative \( v_3 \) shows shear-thinning behavior in nonlinear regime.
Moreover, the ratios between the higher harmonics and first harmonic show the extent of nonlinearity. Thus, as the strain increases, the contribution of the higher harmonics increase. These results are consistent with those Salehiyan et al. who showed that the contribution of higher harmonics for PLA/PC polymer blend nanocomposites increased by increasing in strain amplitude. So, nonlinearity effects become more and more significant as the strain amplitude increases.

Figure S2. Elastic Chebyshev coefficients for neat PVDF and nanocomposites.

Figure S3. Viscous Chebyshev coefficients for neat PVDF and nanocomposites.
Lissajous-Bowditch patterns

Figure S4 presents schematic of Lissajous patterns plots.

![Schematic of Lissajous patterns plots](image)

**Figure S4.** Schematic of Lissajous pattern (a, d) viscous dominated, (b, e) viscoelastic, and (c, f) elastic dominated.

**Dissipated energy**

The area of Lissajous curves, in one cycle, can be used to determine the dissipated energy per unit volume. The dissipated energy is defined by following expression:

\[
E_d = \int_{cycle} \sigma \, dy \quad (1)
\]

Figure S5 shows the total stress versus the strain at strain amplitude of 100%. Based on Eq.1, we can use the area of these graphs to estimate the dissipated energy. As expected, the area of the Lissajous loops increase for binary PNCs compared to neat PVDF, which shows the higher dissipated energy due to the breakdown and rupture of the nanofillers network. A possible source of dissipation is the interfacial slippage on the surface of nanoparticle-matrix.\(^3, 4\) The
adhesion at the interface of nanofiller-polymer at high strain amplitudes is not strong enough to prevent interfacial slip. The other source of dissipation is the rotation of the CNTs clusters and individual CNTs. The better dispersion of CNTs, in hybrid system, leads to increase the number of frictional interactions of nanofiller-nanofiller and nanofiller-matrix. Thus, based on aforementioned mechanisms, the dissipated energy for PVDF/CNT/MnO₂NW is expected to be higher which can be easily seen from the area of the Lissajous curves in Figure S5.

![Elastic Lissajous-Bowditch curves at strain amplitude of 100% for neat PVDF (blue), PVDF/1.0wt%CNT (green), PVDF/2.0wt%MnO₂NW (red), and PVDF/1.0wt%CNT/2.0wt%MnO₂NW (black) nanocomposites.]

**References**


Appendix C– Supplementary information for chapter 5

Supporting Information
for
The Key Role of Processing in Tuning Nonlinear Viscoelastic Properties and Microwave Absorption in CNT-based Polymer Nanocomposites

Milad Kamkar, S. M. Nourin Sultana, Shital Patangrao Pawar, Uttandaraman Sundararaj*

Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr NW, Calgary, Canada T2N 1N4
*Corresponding Author: Tel: +1-403-210-6549, Email: u.sundararaj@ucalgary.ca

Linear rheology (SAOS).

In this section, linear rheology was employed as a strong and well-known tool to investigate the dispersion state and network structure of the nanofillers. Strain sweep dynamic tests in which the sample is subjected to an increasing oscillatory strain amplitudes at a controlled frequency were used to distinguish the linear and the nonlinear viscoelastic regimes. Based on these results (see Figure 5), strain amplitude of 0.1% is small enough for our MWCNT-based polymer nanocomposites to be in linear viscoelastic region (LVR).

Figure S1. Oscillatory amplitude sweep response of nanocomposites containing (a) and (b) 0.5vol.% MWCNT, (c) neat PS (green), and (d) and (e) 2.0vol.% of MWCNT for sample prepared by melt mixing (blue) and solution mixing (red) methods. Open symbols represent loss modulus ($G''$) and solid symbols represents storage modulus ($G'$) for angular frequency of $\omega = 0.1$-500 rad/s at strain amplitudes of $\gamma_0=0.1\%$ using parallel-plate geometry at a gap-size of 0.2mm at 230°C. Data points highlighted by black arrows show crossover frequency at which both moduli are equal $G''=G'$.  

213
The results of small amplitude (0.1%) frequency-sweep dynamic tests on the MWCNT-based polymer nanocomposites are shown in Figure 4. In this test, loss modulus ($G''$) and storage modulus ($G'$) were monitored as a function of frequency ranging from 500 to 0.1 rad/s. As can be seen in Figure 4, addition of only 0.5 vol.% MWCNT leads to deviation from terminal viscoelastic behavior. Additionally, in contrast to viscous dominant behavior of the matrix conjugated with simple dynamics and terminal behavior, a secondary crossover (i.e., frequency at which both moduli are equal $G'' = G'$, highlighted by black arrows) emerges at low-frequency region for nanocomposites containing 0.5 vol.% MWCNTs. The first crossover occurs at higher frequency. The non-terminal behavior accompanied by the emergence of secondary crossover reveal an elastic dominant behavior due to formation of a 3-dimentional MWCNT network structure in our nanocomposite samples.

From the position of the first crossover to the position of secondary crossover $G' < G''$ and after the second crossover $G' > G''$. The first crossover originates from the nature of polymer segmental motions, which is suggestive of typical elastic response in extremely short time scales. However, the secondary crossover at low and intermediate frequencies is a sign of a transition from a viscous-like to a solid-like response at low frequency region (larger relaxation times). Marceau et al.[1] observed the same behavior in PDMS/MWCNT nanocomposites. The authors also showed that this crossover behavior is because of relaxation of individual nanotubes by Brownian motions.

The secondary crossover of solution-mixed nanocomposites occurs at higher frequency compared to nanocomposite prepared by melt mixing method. Moreover, at all MWCNT concentrations, $G'$ value is higher for solution-mixed polymer nanocomposites. The higher $G'$ values and the shift in the secondary crossover to higher frequencies and extension of $G' > G''$ region (which solid behavior is dominant) for solution-mixed sample, is a direct consequence effect of mixing method on MWCNT network structure formation. Hence, the higher
association and direct tube-tube contacts via entanglements in dense clusters in the solution-mixed nanocomposites, the more number of load bearing junctions and entrapped polymer chains, which restrain long-range molecular chain motions and increases the mechanical properties in this sample. Song et al.[2] observed the same behavior and they reported higher $G'$ for systems containing more agglomerates. They postulated, “the agglomerated trap polymer resin in the voids between CNTs and nanocomposite behave as it had lower fraction of polymer matrix”. However, since the CNTs aspect ratio is an important factor to contribute to viscoelastic behavior,[3-5] these differences in rheological properties of solution-mixed and melt-mixed samples cannot be solely ascribed to difference in dispersion state. In our previous work[3], different CNTs with featuring different physical structure were synthesized and then introduced to a polymer matrix. We observed better rheological properties for CNT-based nanocomposites containing longer CNTs. Hence, shorter CNTs are expected in melt-mixed samples due to high applied shear rate on samples during the mixing, leading to lower rheological properties.
Nonlinear rheology (LAOS) for PS/0.5 vol.% MWCNT.

![Graphs showing dynamic viscosities, local elastic measures, and intra-cycle viscoelastic parameters for PS/0.5 vol.% MWCNT.](image1)

Figure S2. Dynamic viscosities (minimum strain rate \( \eta_M' \) and large strain rate \( \eta_L' \) viscosities), local elastic measures (minimum strain \( G_M' \) and large strain \( G_L' \) moduli) and intra-cycle viscoelastic parameters (strain-stiffening ratio \( S \) and shear-thickening ratio \( T \)) for PS/0.5 vol.% MWCNT. Data have been obtained at angular frequency of 0.1 rad/s using parallel-plate geometry at 230 °C.

Nonlinear rheology (LAOS) for PS/1.0 vol.% MWCNT.

![Graphs showing dynamic viscosities, local elastic measures, and intra-cycle viscoelastic parameters for PS/1.0 vol.% MWCNT.](image2)

Figure S3. Dynamic viscosities (minimum strain rate \( \eta_M' \) and large strain rate \( \eta_L' \) viscosities), local elastic measures (minimum strain \( G_M' \) and large strain \( G_L' \) moduli) and intra-cycle viscoelastic parameters (strain-stiffening ratio \( S \) and shear-thickening ratio \( T \)) for PS/1.0 vol.% MWCNT. Data have been obtained at angular frequency of 0.1 rad/s using parallel-plate geometry at 230 °C.
Lissajous–Bowditch curves.

Figure S4 (a), (b), and (c) show the output intra-cycle shear stress signals at different strain amplitudes ($\gamma_0 = 0.15, 150, \text{ and } 1000\%$) for PS/2.0 vol.% MWCNT nanocomposites. Similar behavior was observed for melt- and solution-mixed nanocomposites at higher concentrations of MWCNTs. As can be observed from small amplitude deformation ($\gamma_0 = 0.15\%$) data, the output shear stress response is a single-harmonic sinusoid, which is consistent with a typical linear viscoelastic response, demonstrating all nonlinear contributions are zero. However, significant differences in the value of the maximum shear stress in one cycle of oscillation is observable as the nanocomposite mixing method changes. These differences will be discussed later based on Lissajous-Bowditch loops. Beyond the linear viscoelastic limit, due to the excitation of the higher harmonics, the distortions in stress signal response become apparent. Hence, the output stress signal is entirely non-sinusoidal for all samples at strain amplitude of 150% and 1000% (see Figure S4 (b) and (c)).
Figure S4. (a), (b), and (c) output raw intra-cycle shear stress wave-form, (d), (e), and (f) 3-D Lissajous-Bowditch loops, (g), (h), and (i) Lissajous-Bowditch loops on elastic projection (dotted lines represent elastic stress contribution (τ′)), and (j), (k), and (l) Lissajous-Bowditch loops on viscous projection (dotted lines represent viscous stress contribution (τ″)) for PS/2.0 vol.% MWCNT melt-mixed (blue) and solution-mixed (red) nanocomposites. Data was obtained using a parallel-plate geometry (with a gap-size of 0.2 mm) at 230 °C. Projections on the elastic (τ - γ) and viscous (τ - dγ/dt = γ′) planes are presented at strain amplitudes of γ₀ = 0.15, 150, 1000% and an angular frequency of ω = 1 rad/s.
To investigate the origin of nonlinearity and the effect of processing method on intra-cycle viscoelastic behavior, we used stress decomposition method, which decomposes stress into elastic ($\tau'$) and viscous ($\tau''$) contributions. Elastic stress contribution ($\tau'$) is an odd function of strain ($\gamma(t) = \gamma_0 \sin \omega t$) and viscous stress contribution ($\tau''$) should be odd in strain rate ($\dot{\gamma}(t) = \dot{\gamma}_0 \cos \omega t$).[6, 7] The visual depiction of total shear stress ($\tau$) as a function of strain ($\gamma$) or strain rate ($\dot{\gamma}$) in one cycle can be presented by Lissajous-Bowditch loops (will be called Lissajous loops for simplification). Figure S4 (d), (e), and (f) show the 3-D Lissajous loops ($\tau_{raw}$ vs. $\gamma_{raw}$ and $\dot{\gamma}_{raw}$) at strain amplitudes of $\gamma_0 = 0.15$, 150, 1000%, respectively. In linear region for a perfectly elastic system, the input strain deformation and output shear stress waveform superimpose and the resulting Lissajous loops would be a line in elastic projection (see Figure S4 of Supporting Information in our previous work[8]). While, pure viscous system shows an opposite behavior. So, an ellipsoidal-shaped pattern in Lissajous loop is expected in both elastic and viscous projections for viscoelastic materials in the linear region. It should be mentioned, not only Lissajous curves help in distinguishing the linear and nonlinear viscoelastic regions, but also one can easily assess the type of intra-cycle viscoelastic nonlinearity. Hence, Lissajous curves provide a compact way of displaying oscillatory data.

Figure S4 (g), (h), and (i) compare elastic Lissajous curves of polymer nanocomposites. In linear framework (e.g., $\gamma_0 = 0.15\%$), Lissajous curves show a symmetric ellipsoidal shape. Moreover, as can be seen in Figure S4 (a), elastic stress contribution ($\tau'$) is a straight line for samples, which means that the higher harmonics do not exist in output stress waveform. Increasing the applied strain amplitude leads to emergence of higher harmonics and a clear distortion can be discerned with ease in Lissajous curves and elastic stress contribution ($\tau'$) (the elastic stress contribution ($\tau'$) turns into a curvy line), indicating nonlinear viscoelastic framework. Moreover, in line with Figure 6, the upward convex of the elastic stress
contribution ($\tau'$) reveals occurrence of intra-cycle strain-stiffening nonlinearity in MWCNT-based polymer nanocomposites.

The effects of processing method on viscoelasticity of the nanocomposite samples can be easily noticed in Lissajous curves and the corresponding stress contributions. The slope of the elastic stress and the area of the ellipses (in elastic projection) are different for melt-mixed and solution-mixed nanocomposite, which stems from differences in their microstructure. The slope of $\tau'$ in the linear viscoelastic region represent storage modulus ($G'$). The higher slope of elastic stress ($\tau'$) in small amplitude region ($\gamma_0 = 0.15\%$) for solution-mixed sample, indicates greater $G'$ for this nanocomposite compared to melt-mixed sample (this is in concert with results of the Figure S1 and Figure 4). Moreover, the maximum shear stress ($\tau_{\text{raw}}\)_{\text{max}}$ of melt-mixed sample in strain amplitudes of $\gamma_0 = 0.15$, 150, and 1000% is 21 Pa, 2010 Pa, and 4205 Pa, respectively. Whereas, ($\tau_{\text{raw}}\)_{\text{max}}$ significantly increased to 236 Pa, 3750 Pa, and 6020 Pa for solution-mixed sample at the corresponding deformations.

Figure S4 (g), (h), and (i) depict viscous Lissajous curves of polymer nanocomposites. In concert with elastic Lissajous curves, for samples prepared by solution mixing method dynamic viscosity is higher in linear region (higher slope of viscous stress ($\tau''$) in linear region, i.e., $\gamma_0 = 0.15\%$) and nonlinearity occurs more extensively in nonlinear framework. That is, the distortion of viscous Lissajous loops and curvature of viscous stress ($\tau''$) of the solution-mixed sample is more noticeable compared to melt-mixed method. For instance, the higher downward concavity of viscous stress ($\tau''$) at $\gamma_0 = 150\%$ for solution-mixed nanocomposite demonstrates that intra-cycle shear-thinning behavior is stronger for this sample.

It is worth pointing out that the higher distortion of the Lissajous curves and higher deviation from linearity in shear stress contributions for solution-mixed sample is consistent with our previous findings,[8] where we observed higher viscoelastic nonlinearity for the
systems with a more stiffer nanofillers network. The differences in the nonlinear viscoelasticity of melt- and solution-mixed samples are more noticeable in viscous projection of Lissajous curves where a clear self-intersection in the total shear stress curve at strain amplitude of $\gamma = 1000\%$ occurs for solution-mixed nanocomposite. This behavior indicates a strong nonlinearity in solution-mixed nanocomposite (see Figure S5 for better resolution).

Several authors have reported the emergence of self-intersection under LAOS field for different systems.[3, 7, 9, 10]. In a recent work, Goudoulas et al.[10] provided a detailed explanation of self-intersection in a polymeric solution. Ewoldt et al.[11] showed that the self-intersection in the viscous projection of Lissajous loops is accompanied by a strong elastic nonlinearity (emergence of a maxima) in the same quadrant of the deformation cycle in the elastic projection curves. Figure S5 shows the existence of the maxima in elastic projection with a better resolution (star and triangle symbols in each half cycle of oscillation). This is similar to the stress overshoot response during the start-up of the steady shear flow. After this local overshoot, system begins to flow, which in turn, leads nanofillers network rupture and nanofillers orientation under sufficiently large shear rate associated with large deformation and, thus, the total stress decreases.

Figure S5. Elastic and viscous Lissajous–Bowditch curve co-plotted with intra-cycle stress waveform for solution-mixed PS/2.0 vol.%MWCNT at $\gamma_0 = 1000\%$ and $\omega = 1$ rad/s. Highlighted black points shows half cycle of oscillation on the intra-cycle shear stress waveform and the highlighted red points shows the corresponding data on viscous and elastic Lissajous–Bowditch trajectories. Circle and triangle symbols depict the position of maximum stress in half cycle of oscillation.
References


Appendix D– Supplementary information for chapter 6

Supplementary information for

On the Viscoelastic Response of Covalently Cross-linked Gelatin Methacryloyl (GelMA) Hydrogel under Large Shear Deformations

Milad Kamkar\textsuperscript{a}, Mohsen Jannamalkei\textsuperscript{b}, Amir Sanati-Nezhad\textsuperscript{b}, Uttandaraman Sundararaj\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a} Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr NW, Calgary, Canada T2N 1N4
\textsuperscript{b} BioMEMS and Bioinspired Microfluidic Laboratory, Department of Mechanical and Manufacturing Engineering, University of Calgary, Calgary, Canada

*Corresponding Author: Tel: +1-403-210-6549, Email: u.sundararaj@ucalgary.ca

\textbf{Degree of methacrylation.} The degree of methacrylation or the degree of functionalization (DOF) is known as a key parameter in tailoring the mechanical properties of GelMA. The DOF was evaluated by the proton nuclear magnetic resonance (\(1\,\text{H}\,\text{NMR}\)) at the frequency of 400 MHz using a Bruker AVANCE III NMR spectrometer with a BBFO probe (Bruker, Billerica, MA, USA). Briefly, 20 mg of GelMA precursor or gelatin powder was dissolved in 1 ml of deuterium oxide (Cambridge Isotope Laboratories Inc, MA). The recorded spectra were analyzed by Bruker TopSpin software. To normalize amine signals (2.8–2.95 ppm), the phenylalanine signals (7.2–7.5 ppm) were considered as the internal reference. The DOF of GelMA in hydrogels was estimated based on the following equation:

\[
\text{DOF} = \left(1 - \frac{\text{Lysine integration signal of GelMA}}{\text{Lysine integration signal of Gelatin}}\right) \times 100
\]

Free amine groups on gelatin only bound to the methacrylate groups. Therefore, DOF can be evaluated by comparing the integration signal of amino lysine (highlighted in blue in Figure S1) in gelatin and GelMA. While, the phenylalanine signals (highlighted in yellow in Figure S1) was considered as the internal reference. Obviously, the amount of amino lysine in GelMA product remarkably decreased comparing to gelatin. Based on the above mentioned equation, the DOF of GelMA was estimated to be 63%.
Figure S1. The 1H-NMR spectra of GelMA and gelatin. H-NMR spectra were collected at room temperature in deionized water at a frequency of 400 MHz using a Bruker AVANCE III NMR spectrometer with a BBFO probe.

**Surface coverage of TMSPMA coating on glass slides.** To evaluate the TMSPMA coating in detail, atomic force microscopy (AFM) was used. A commercial AFM (NanoIR2-ANASYS Instrument Inc) with tapping mode cantilever was used to visualize the surface topography of substrates in nano-scale. The samples were thoroughly washed with ethanol and nitrogen dried prior scanning. While TMSPMA coated slides possessed an rms roughness of 6.59 nm, AFM revealed a relatively flat surface for the bare glass slide with an rms roughness of 0.16 nm (Figure S2 (a) and (b)). The topographical properties of the slides are summarized in table shown in Figure S2 which could be used as a measure for future studies. Reconstructed 3D-images from the topographies are also shown in Figure S2 (c) and (d), which evidently proves the presence of various clusters. The clusters and the consequent roughness are developed by the formation of methacrylate sites on the slide surface. By using Gwyddion free software, the surface coverage of the methacrylate function groups on slides was estimated to be 58.6±4.7%.
Background. Under a small input oscillatory deformation, $\gamma = \gamma_0 \sin(\omega t)$, the output shear stress is a simple cosine function of the frequency (see Figure S3 (a), raw stress values in a cycle in linear regime). Once materials enter the nonlinear framework associated with an oscillatory shear flow, i.e., large amplitude oscillatory shear (LAOS) flow, the output shear stress waveform becomes distorted and cannot be defined by a simple sinusoidal function anymore. Hence, under LAOS flow, the input sinusoidal strain signal is translated to a non-sinusoidal stress signal (see Figure S3 (b)). In this condition, since the nonlinear shear stress response is not a single-harmonic sinusoid, loss modulus ($G''$) and storage modulus ($G'$) are strain-dependent and can no longer sufficiently describe the nonlinear mechanical response.\textsuperscript{1,2}

The nonlinearity of the stress waveform can be noted easier in Lissajous–Bowditch curves which shows raw stress values against raw strain values in one cycle of oscillation (see Figure S3 (d), Lissajous–Bowditch plots in elastic projection). Lissajous–Bowditch plots can deliver more meaningful information. Based on the viscoelastic theories, since both stress and strain waveforms superimpose in linear region, the Lissajous–Bowditch shapes are ellipsoidal for...
viscoelastic materials (Figure S3 (c)). Emergence of any distortion in ellipsoidal shape of Lissajous–Bowditch plots reveals occurrence of nonlinearity as a result of excitation of higher harmonics in output stress waveform (see Figure S3 (d) where the Lissajous–Bowditch plot is distorted). Therefore, in nonlinear regime, the first harmonic measures are insufficient to characterize the complex nature of the nonlinear mechanical behavior of materials.

Several methods, such as stress decomposition\(^1\) and FT-rheology\(^3\) have been used to analyze the distorted stress waveform in nonlinear viscoelastic framework. For example, the viscoelastic shear stress \(\sigma\) response to an input oscillatory strain at steady-state condition can be written as an in-phase component and an out-phase component and represented as a time-domain Fourier series of odd harmonics\(^4\):

\[
\sigma(t) = \gamma_0 \sum_{n=1}^{N} \left[ G'_n(\omega, \gamma_0) \sin(n\omega t) + G''_n(\omega, \gamma_0) \cos(n\omega t) \right] \quad (1)
\]

where \(\gamma_0\) is strain amplitude, \(G'_n\) and \(G''_n\) are amplitudes of \(n\) harmonics with frequencies \((n\omega)\).

For materials in the linear viscoelastic region, the output stress signals are a sinusoidal wave,
which can be simply characterized by only the first harmonic coefficient, \( n = 1 \), with a temporal phase shift \( \delta_1 = G''_1/G'_1 \). The appearance of higher order harmonics indicates nonlinearity in the viscoelastic behavior, meaning that it cannot be described simply by sinusoidal waves. Moreover, in the nonlinear regime, the measured \( G' \) and \( G'' \) moduli do not have a clear physical meaning, which means another method must be applied to interpret the stress signal. Thus, we used the following method to describe the physical meaning of nonlinear parameters.

The stress response \( (\sigma(t)) \) can be decomposed into an elastic stress component \( (\sigma') \) and a viscose stress component \( (\sigma'') \) as an odd function of normalized strain \( (x(t) = \frac{y(t)}{y_0}) \) and normalized strain rate \( (y(t) = \frac{\dot{y}(t)}{y_0}) \) respectively. Thus, the total stress can be expressed as:

\[
\sigma(t) = \sigma'(t) + \sigma''(t) \tag{2}
\]

Ewoldt et al.\(^5\) showed that the elastic \( (\sigma') \) and viscous \( (\sigma'') \) stress contributions can be fitted by a series of Chebyshev polynomials of the first kind \( (T_n) \) in the orthogonal space as follow:

\[
\sigma'(x; \omega, \gamma_0) = \gamma_0 \sum e_n(\omega, \gamma_0) T_n(x) \tag{3},
\]
\[
\sigma''(y; \omega, \gamma_0) = \gamma_0 \sum v_n(\omega, \gamma_0) T_n(y) \tag{4},
\]

where \( x \) is normalized strain \( \frac{y(t)}{y_0} \), \( y \) is normalized strain rate \( \frac{\dot{y}(t)}{y_0} \), and “e” and “v” are Chebyshev weighting coefficients and represent intra-cycle elastic and viscous behavior, respectively. The authors also introduced local dynamic viscosities (minimum-strain rate viscosity, \( \frac{d\sigma}{d\gamma} \bigg|_{\gamma=0} \equiv \eta'_M \), and large-strain rate viscosity, \( \frac{d\sigma}{d\gamma} \bigg|_{\gamma=\pm y_0} \equiv \eta'_L \)) and local moduli (minimum-strain modulus, \( \frac{d\sigma}{d\gamma} \bigg|_{\gamma=0} \equiv G'_M \), and large-strain modulus, \( \frac{d\sigma}{d\gamma} \bigg|_{\gamma=\pm y_0} \equiv G'_L \)). Figures S2 (c) and (d) show the graphical illustration of \( G'_M \) and \( G'_L \). In linear region, both \( G'_M \) and \( G'_L \) are equal and converge to linear elastic modulus, i.e., \( G'_M = G'_L = G' \) (see Figure S3 (c)). However, in the nonlinear region, \( G'_M \) and \( G'_L \) are not equal as a result of emergence of higher harmonics,
and their relative values dictates the type of elastic intra-cycle nonlinearity. Similarly, by comparing the behavior of $\eta'_M$ and $\eta'_L$, one can recognize the type of viscous intra-cycle nonlinearity. Through the defined nonlinear parameters, Ewoldt et al.\textsuperscript{5} introduced strain-stiffening ratio ($S = \frac{G' - G'_M}{G'_L}$) and shear-thickening ratio ($T = \frac{\eta' - \eta'_M}{\eta'_L}$). The type of intra-cycle nonlinear viscoelastic behavior can be described by the sign of $S$ and $T$ indices. Table S1 and Table S2 summarize nonlinear parameters and provide a guideline for recognizing the type of nonlinearity based on the defined parameters.

### Table S12-1. Characterizing elastic nonlinearity in response to imposed oscillatory shear deformation.\textsuperscript{5}

<table>
<thead>
<tr>
<th>Elastic parameters</th>
<th>Inter-cycle</th>
<th>Intra-cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Both $G'_M$ and $G'_L$ increase with increasing $\gamma_0$</td>
<td>Inter-cycle strain stiffening</td>
<td>-</td>
</tr>
<tr>
<td>Both $G'_M$ and $G'_L$ decrease with increasing $\gamma_0$</td>
<td>Inter-cycle strain softening</td>
<td>-</td>
</tr>
<tr>
<td>$S &gt; 0$ at each strain</td>
<td>-</td>
<td>Intra-cycle strain stiffening</td>
</tr>
<tr>
<td>$S = 0$</td>
<td>Linear behavior</td>
<td>Linear behavior</td>
</tr>
<tr>
<td>$S &lt; 0$ at each strain</td>
<td>-</td>
<td>Intra-cycle strain softening</td>
</tr>
<tr>
<td>$v_3 &gt; 0$</td>
<td>-</td>
<td>Intra-cycle strain stiffening</td>
</tr>
<tr>
<td>$v_3 = 0$</td>
<td>Linear behavior</td>
<td>Linear behavior</td>
</tr>
<tr>
<td>$v_3 &lt; 0$</td>
<td>-</td>
<td>Intra-cycle strain softening</td>
</tr>
</tbody>
</table>

### Table S12-2. Characterizing viscous nonlinearity in response to imposed oscillatory shear deformation.\textsuperscript{5}

<table>
<thead>
<tr>
<th>Viscous parameters</th>
<th>Inter-cycle</th>
<th>Intra-cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Both $\eta'_M$ and $\eta'_L$ increase with increasing $\gamma_0$</td>
<td>Inter-cycle shear thickening</td>
<td>-</td>
</tr>
<tr>
<td>Both $\eta'_M$ and $\eta'_L$ decrease with increasing $\gamma_0$</td>
<td>Inter-cycle shear thinning</td>
<td>-</td>
</tr>
<tr>
<td>$T &gt; 0$ at each strain</td>
<td>-</td>
<td>Intra-cycle shear thickening</td>
</tr>
<tr>
<td>$T = 0$</td>
<td>Linear behavior</td>
<td>Linear behavior</td>
</tr>
<tr>
<td>$T &lt; 0$ at each strain</td>
<td>-</td>
<td>Intra-cycle shear thinning</td>
</tr>
<tr>
<td>$v_3 &gt; 0$</td>
<td>-</td>
<td>Intra-cycle shear thickening</td>
</tr>
<tr>
<td>$v_3 = 0$</td>
<td>Linear behavior</td>
<td>Linear behavior</td>
</tr>
<tr>
<td>$v_3 &lt; 0$</td>
<td>-</td>
<td>Intra-cycle shear thinning</td>
</tr>
</tbody>
</table>

Previous reports in the literature\textsuperscript{6-8} mainly used rheometry as a tool to define the linear viscoelastic regime (LVR) using stress or strain sweep in order to monitor the kinetic of the gelation (using time sweep), and/or study the mechanical response in linear framework (using frequency sweep). However, there are few works in literature concerning nonlinear response of biopolymer networks. For instance, Kurniawan et al.\textsuperscript{9} utilized LAOS measurements to
investigate nonlinearity of self-assembled type-I collagen. Authors did not report the viscous nonlinearity as they claimed that collagen networks are predominantly elastic. In this study, we aim to provide an in-depth understanding and a detailed explanation of mechanical response of the permanently (covalently) cross-linked GelMA hydrogels in the nonlinear viscoelastic regime. We also observed strong viscous nonlinearity in both medium amplitude and large amplitude regions, indicating the vital role of viscous nonlinear response in permanently cross-linked GelMA hydrogels. To the best of our knowledge, there is no study in the literature that systematically investigates the physical structure of permanently cross-linked gelatin-based hydrogels at different gelatin contents via nonlinear viscoelastic parameters under large deformations. Rheological Lissajous–Bowditch loops and plots of the nonlinear viscoelastic parameters are presented to characterize the type and origin of nonlinearity in the chemically cured gelatin-based hydrogels. These insights have important implications for the rational development of hydrogel-based biomaterials for designing of biocompatible scaffolds in tissue engineering applications.

**Linear viscoelastic characterization.** In this section, frequency sweep test was used to investigate the effect of GelMA concentration and network structure on dynamic viscoelastic response of the hydrogels in the linear regime. Figure S4 (a), (b), and (c) show the frequency dependence of shear storage modulus ($G'$) and shear loss modulus ($G''$) over a broad range of frequency ranging 100 to 0.01 s$^{-1}$. Over this range of frequency, $G'$ is several orders of magnitude greater than $G''$. This verifies that the GelMA hydrogel has predominantly elastic character. This confirms that the deformation energy is stored in the elastic stretching of the molecules. This is in agreement with previous findings in the literature, which studied the viscoelastic behavior of gelatin-based hydrogels under small deformation in linear viscoelastic framework. Moreover, $G'$ is independent of frequency (plateau modulus) and $G''$
demonstrates insignificant variation upon changes in frequency, which is an indication of typical viscoelastic response of permanently cross-linked chemical gels.

The elastic modulus of the hydrogels depends on the number of cross-links, length, and stiffness of the chains between the cross-link sites. Hence, increasing the concentration of the GelMA from 10% to 20% (w/v) elevated the $G'$ value from about 2kPa to 10kPa. This is a direct consequence of structural differences in samples and formation of a more homogenous network with the increase in polymer content (see Figure 2 of the main manuscript). The change in linear elastic modulus due to increasing the polymer content implies sensitivity of $G'$ to any change in topology of the network (e.g., fraction of elastically effective chains).

---

**Figure S4.** Storage modulus ($G'$) and loss modulus ($G''$) of GelMA hydrogels as a function of frequency at strain amplitude of 1% using parallel-plate geometry at room temperature for (a) 10% (w/v) GelMA hydrogel, (b) 15% (w/v) GelMA hydrogel, and (c) 20% (w/v) GelMA hydrogel. (d) complex viscosity ($\eta^*$) as a function of frequency, and (e) tan $\delta$ as a function of frequency. (f) the schematic shows coexistence of physical and chemical cross-links in GelMA hydrogels. The GelMA hydrogel contains –NH$_2$ and –OH groups, which can form hydrogen bonding (see Schemes 1 and 2).
Figure S4 (d) shows the behavior of the complex viscosity ($\eta^*$) of the hydrogels as a function of frequency. It has been shown that $\log(\eta^*)$ and $\log(\omega)$ has a negative linear relationship with slope of -1 for a perfectly covalent cross-linking network.$^{12-13}$ This relationship indicates an infinite relaxation time compared to the experimental time scale. Hence, a negative slope of -1 over the probed frequency range reveals the formation of a perfect elastic network of GelMA in all hydrogels. Taken together, these results indicate that all samples are extensively interconnected as a result of strong chemical bonds formed during photo-curing.

Interestingly, the value of $G''$ increases with the decrease in the frequency. The increase of $G''$ at lower frequencies demonstrates that, as the experiment time increases, relaxation modes of the polymer segments are activated, caused by internal motions within the cross-links. The damping factor ($\tan \delta = G''/G'$) is plotted in Figure S4 (e). For all the GelMA hydrogels, $\tan \delta$ is independent of frequency (plateau at high frequency region) and it increases by decreasing the frequency below a critical strain frequency. At high enough frequencies, the relaxation process of the network is not fast enough to dissipate the shear stress energy instantly; therefore, $\tan \delta$ is independent of frequency. However, in low frequency region, the hydrogel network can dissipate the external energy and, thus, $\tan \delta$ increases, indicating a weak dynamic for these hydrogels at longer time scales.

Zou et al.$^{13}$ compared the linear viscoelastic properties of a dual cross-linked (DC) hydrogel (featuring both physical and covalent cross-links) and a singly chemically (SC) cross-linked hydrogel. They observed distinctly different behavior in $\tan \delta$ of DC and SC hydrogels; $\tan \delta$ decreased for DC hydrogels and increased for SC hydrogels with increasing strain frequency. Hence, based on the literature results and $\tan \delta$ curve in Figure S4 (e), we concluded that our GelMA hydrogel has a DC nature. Figure S4 shows the dramatic growth of the $G'$ for the uncured GelMA hydrogel after cessation of the start-up shear flow. These results also
confirm the existence of physical cross-links in our systems. The schematic in Figure S5 (f) shows the dual cross-linked nature of GelMA hydrogel, i.e., coexistence of covalent (chemical) cross-links and physical cross-links (e.g., hydrogen bonding) among the polymer chains. These results are used in the main manuscript to interpret the nonlinear viscoelastic behavior of the GelMA hydrogels.

Herein, we provide a thorough picture of linear viscoelastic response of GelMA hydrogels containing different concentrations of the polymer. We show that linear viscoelastic measurement is a powerful tool to characterize the physical structure of the hydrogels. However, aforementioned, in real conditions, e.g., in the human body, biomaterials experience large and rapid deformations and fall into nonlinear viscoelastic regime, thus, necessitating an in-depth investigation of the nonlinear behavior of hydrogels.

**Time sweep test immediately after start-up shear flow.** Figure S5 depicts the evaluation of the normalized storage modulus ($G' / G'_{\text{max}}$) after start-up shear test at shear rate of $1 \text{ s}^{-1}$ for uncured GelMA hydrogel. Employing steady shear on uncured hydrogel leads to the rupture of the network formed by physical links. During this time, the chains undergo orientation to the flow direction. Based on Figure S5, the growth of storage modules for the times after cessation of steady shear flow reveals occurrence of gelation, which has physical origin.

![Figure S5. Evaluation of storage modulus ($G'$) of uncured 10% (w/v) hydrogel immediately after start-up shear test at shear rate of $1 \text{ s}^{-1}$.](image)
Yield stress.

![Yield stress graph](image)

Figure S6. Yield stress for 10%, 15%, and 20% (w/v) hydrogels.

Rupture force under extensional mode for cross-linked 10% (w/v) GelMA attached to glass slide.

![Extensional force graph](image)

Figure S7. Extensional force vs time at the extensional rate of 0.05mm/s for 10% (w/v) GelMA hydrogel.

Rupture Stress under simple shear deformation for cross-linked 10% (w/v) GelMA attached to glass slide.

![Shear Stress graph](image)

Figure S8. Shear Stress vs time at the shear rate of 0.25s⁻¹ for 10% (w/v) GelMA hydrogel.
Phase angle ($\delta$) versus strain amplitude ($\gamma_0$).

Figure S9. Phase angle ($\delta$) versus strain amplitude ($\gamma_0$) for GelMA hydrogels during strain sweep experiments. The angular frequency was 1 rad/s.

Degree of strain hardening.

Degree of strain hardening for GelMA hydrogels at different polymer concentrations during strain sweep experiments. The angular frequency was 1 rad/s.

Maximum shear stress in one cycle at strain amplitude of 70%.

Figure S11. Maximum shear stress in one cycle at strain amplitude of $\gamma_0 = 70\%$ for 10%, 15%, and 20% (w/v) hydrogels. The angular frequency was 1 rad/s.
Shear-thickening index of uncured hydrogel.

Figure S12. Intra-cycle viscoelastic parameter: shear-thickening ratio ($T$) of uncured hydrogel containing 10% (w/v) GelMA. The angular frequency was 1 rad/s.

Comparison of viscoelastic behavior of hydrogel with and without attaching to glass slide.

Figure S13 presents the viscoelastic behavior of the attached GelMA hydrogel, chemically linked to the glass plates and then attached with a double-sided tape to the rheometer plates, and unattached GelMA hydrogel, without glass plates. Dramatic differences in the rheological behavior of the samples is observed, even in small amplitudes, which potentially stem from poor stress transfer to the unattached sample due to the weak adhesion at hydrogel-metal plates interface. Based on Figure 3 of the manuscript, GelMA hydrogels attached to the rheometer plates exhibit type II behavior (strain-hardening), both $G'$ and $G''$ increase, an then it yields at strain amplitude of $\gamma_0 = 100\%$ (green circle symbol in Figure S13). This yielding is a direct consequence of rupture of the bulk of the GelMA hydrogel (see the inset c' in Figure S13). However, GelMA with non-robust attachment to the rheometer plates obeys an entirely different scenario. That is, the mentioned sample shows type III behavior (weak strain overshoot), $G'$ decreases while $G''$ first increases and then decreases. Moreover, no rupture occurred in the bulk of the sample and the GelMA remained intact after running the strain sweep test and experiencing a deformation as large as $\gamma_0 = 1000\%$ (compare the insets a' and b' in Figure S13). These results verify that yielding of the unattached sample is mainly because
of the slip at the GelMA-metal plate interface. Hence, the inter-cycle viscoelastic response of the attached and unattached hydrogels is extremely different.

In line with inter-cycle viscoelastic response, there are discrepancies in intra-cycle viscoelastic response of the attached and unattached hydrogels (see Figure S13 (b)-(g)). That is, the onset of both viscous and elastic nonlinearities occurs at smaller strain amplitudes for attached hydrogel. For instance, strain amplitude at which intra-cycle strain stiffening occurs is $\gamma_0 = 40\%$ and is $\gamma_0 = 140\%$ for attached and unattached hydrogel, respectively. Similarly, both intra-cycle shear-thickening behavior and intra-cycle shear thinning behavior start at lower strain amplitudes for attached hydrogel compare to its unattached counterpart. These results reveal the importance of the wall-slip phenomenon in hydrogels containing large fraction of water. Therefore, we cannot capture the real viscoelastic behavior of the hydrogels, especially in large deformations, without overcoming the wall-slip. These results show that viscoelastic data of unattached hydrogels are highly afflicted by artefacts, even at small deformations, due to the wall-slip phenomenon. Hence, the results of the previous works in literature where wall-slip phenomenon was not taken into account, are not accurate in many cases. Figure S14 of Supporting Information shows the intra-cycle viscoelastic difference between attached and unattached samples based on Lissajous loops.
Figure S13. (a) comparison of shear storage ($G'$) (red symbol) and shear loss modulus ($G''$) (black symbol) at an angular frequency of $\omega = 1\text{rad/s}$ for 10\% (w/v) GelMA hydrogel attached to the glass slide (filled symbol) and unattached hydrogel (open symbols). Green circle indicates strain amplitude at which the hydrogel chemically attached to the glass plate yields. $a'$ and $b'$ show the hydrogel without glass slide before and after the amplitude sweep test, respectively. $c'$ shows the hydrogel chemically attached to the glass slide after the amplitude sweep test. (b)-(d) nonlinear viscoelastic parameters for hydrogel chemically attached to the glass slide, (e)-(g) nonlinear viscoelastic parameters for unattached hydrogel.

Comparison of Lissajous-Bowditch plots of hydrogel with and without attaching to glass slide. Figure S14 compares the Lissajous loops of attached and unattached hydrogel. As can be seen in Figure S14, the maximum stress in this cycle of oscillation ($\gamma_0 = 100\%$) increases from 125 Pa for unattached sample to 2650 Pa for attached sample. This significant increase is
a direct consequence of absence of wall-slip and good stress transfer in the attached sample. Moreover, there is a clear distortion in the elastic projection of the attached sample, while no distortion is observable for unattached sample (see the inset for better resolution). This is in line with previous section, which we showed that the intra-cycle nonlinearity occurs sooner for attached sample.

![Figure S14](image)

**Figure S14.** 3-D Lissajous-Bowditch curves and their viscous and elastic projections for attached and unattached 10% (w/v) GelMA hydrogel at strain amplitude of $\gamma_0 = 100\%$ and an angular frequency of $\omega = 1\text{rad/s}$. The inset shows the elastic projection of the unattached sample with better resolution.

**Viscoelastic behavior of hydrogels on unattached glass slides.** Figure S15 shows the strain amplitude sweep results for 10% (w/v) GelMA hydrogel on unattached glass slides. To run this test, the metal plates of parallel-plate geometry were covered by glass slides using a double sided tape. However there was no chemical bonding between the hydrogels and glass slides. Hence, these results are highly afflicted by slippage of hydrogels on the glass slides.

![Figure S15](image)

**Figure S15.** Storage ($G'$) and loss modulus ($G''$) at an angular frequency of $\omega = 1\text{rad/s}$ for 10% (w/v) GelMA hydrogel on unattached glass slides.
References.


Appendix E– Supplementary information for chapter 7

Supporting Information

For

Outstanding Interfacial Viscoelasticity of Graphene Oxide/Air and Graphene Oxide/Oil: A Comparative Study

Milad Kamkar, a&b Farbod Sharif, b Aadithya Kannan,a Gerald G. Fuller, a Uttandaraman Sundararaj b

a Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr NW, Calgary, Alberta T2N 1N4 Canada
b Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025, USA
*Corresponding Author: Tel: +1-403-210-6549, Email: u.sundararaj@ucalgary.ca

Interfacial film development.

Figure S1. (a) and (b) evolution of interfacial elastic ($G'_s$) and loss ($G''_s$) moduli of aqueous suspension of GO at air and oil interfaces at 0.04 and 0.2vol% of GO. Time sweep test has been conducted instantly after loading the sample at strain amplitude of $\gamma_0 = 0.1\%$ and angular frequency of $\omega = 0.5\text{rad/s}$. 

0.04vol.%GO

0.2vol.%GO

Figure S1. (a) and (b) evolution of interfacial elastic ($G'_s$) and loss ($G''_s$) moduli of aqueous suspension of GO at air and oil interfaces at 0.04 and 0.2vol% of GO. Time sweep test has been conducted instantly after loading the sample at strain amplitude of $\gamma_0 = 0.1\%$ and angular frequency of $\omega = 0.5\text{rad/s}$. 
Interfacial Linear viscoelastic parameter of water-GO/air and water-GO/oil.

Figure S2. Linear viscoelastic parameters (elastic ($G'$) modulus, loss ($G''$) and complex viscosity $|\eta^*|$) of water-GO/air and water-GO/oil at different GO concentrations as a function angular frequency at strain amplitude of $\gamma_0 = 0.1\%$. The rheological tests have been conducted at ambient temperature using a du Noüy interfacial geometry.
Nonlinear Viscoelastic behavior of GO film at air and water interfaces (strain sweep test).

Figure S3. Interfacial elastic (\(G'_s\)) and loss (\(G''_s\)) moduli of aqueous suspension of GO at (a) and (b) air and (c) and (d) oil interfaces at 0.04 and 0.2vol% of GO as a function of strain amplitude at angular frequency of \(\omega = 1.0\text{rad/s}\). The rheological tests have been conducted at ambient temperature using a du Noüy interfacial geometry.
Appendix F– Copyrights

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

BACK

CLOSE WINDOW
License Details

This Agreement between University of Calgary – Milad Kamkar ("You") and AIP Publishing ("AIP Publishing") consists of your license details and the terms and conditions provided by AIP Publishing and Copyright Clearance Center.

<table>
<thead>
<tr>
<th>License Number</th>
<th>4736170440577</th>
</tr>
</thead>
<tbody>
<tr>
<td>License date</td>
<td>Dec 26, 2019</td>
</tr>
<tr>
<td>Licensed Content Publisher</td>
<td>AIP Publishing</td>
</tr>
<tr>
<td>Licensed Content Publication</td>
<td>Physics of Fluids</td>
</tr>
<tr>
<td>Licensed Content Title</td>
<td>Application of nonlinear rheology to assess the effect of secondary nanotubes on network structure of hybrid polymer nanocomposites</td>
</tr>
<tr>
<td>Licensed Content Author</td>
<td>Milad Kamkar, Ehsan Allahbadi, Ali Shayesteh Zarei, et al</td>
</tr>
<tr>
<td>Licensed Content Date</td>
<td>Feb 1, 2016</td>
</tr>
<tr>
<td>Licensed Content Volume</td>
<td>30</td>
</tr>
<tr>
<td>Licensed Content Issue</td>
<td>2</td>
</tr>
<tr>
<td>Type of Use</td>
<td>Thesis/Dissertation</td>
</tr>
<tr>
<td>Requestor type</td>
<td>Author (original article)</td>
</tr>
<tr>
<td>Format</td>
<td>Print and electronic</td>
</tr>
<tr>
<td>Portion</td>
<td>Excerpt (&gt; 600 words)</td>
</tr>
<tr>
<td>Will you be translating?</td>
<td>No</td>
</tr>
<tr>
<td>Title of your thesis/dissertation</td>
<td>Large Amplitude Oscillatory Shear Flow: Microstructural Assessment of Polymer Nanocomposites, Hydrogels, and Interfaces</td>
</tr>
<tr>
<td>Estimated completion date</td>
<td>Feb 2020</td>
</tr>
<tr>
<td>Estimated size (number of pages)</td>
<td>240</td>
</tr>
<tr>
<td>Expected completion date</td>
<td></td>
</tr>
<tr>
<td>Requestor Location</td>
<td>University of Calgary</td>
</tr>
<tr>
<td></td>
<td>Department of Chemical and Petroleum Eng</td>
</tr>
<tr>
<td></td>
<td>University of Calgary, 2500 University</td>
</tr>
<tr>
<td></td>
<td>Calgary, AB T2N 1N4</td>
</tr>
<tr>
<td></td>
<td>Canada</td>
</tr>
<tr>
<td></td>
<td>Auth: Milad Kamkar</td>
</tr>
<tr>
<td></td>
<td>0.00 USD</td>
</tr>
</tbody>
</table>

BACK
The key role of processing in tuning nonlinear viscoelastic properties and microwave absorption in CNT-based polymer nanocomposites

Author:
Milad Kamkar, S.M. Nourin Sultan, Shital Patangrao Pawar, Afrooz Eshraghian, Elnaz Erfanian, Uttandaraman Sundararaj

Publication: Materials Today Communications
Publisher: Elsevier
Date: September 2020

© 2020 Elsevier Ltd. All rights reserved.