

Viscoelastic Properties of CNT-PC Compounds: Effect of Compounding Method, CNT Type and Testing Protocol

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Viscoelastic Properties of CNT-PC Compounds: Effect of Compounding Method, CNT Type and Testing Protocol

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Abstract

Frequency-dependent viscoelastic properties are used to elucidate the relationships among the method of compounding, the types of carbon nanotubes (CNT) used within the CNT-polycarbonate composite, the changes in structure (CNT-polycarbonate interaction) and molecular weight of the base polycarbonate. CNT-polycarbonate interaction increases with increasing CNT content and CNT aspect ratio. Addition of the CNT to a TSE at entry ports after attainment of a polycarbonate melt provides higher CNT-polycarbonate interaction. Increasing twin screw extruder residence time by using multiple passes significantly decreases the molecular weight of the polycarbonate within the CNT-polycarbonate composite. This effect is attributed to chain-scission that is intensified by the presence of the CNT-polycarbonate interaction.

Introduction

Considerable activity has been focused on the development of carbon nanotube-polymer composites. One area of focus is the attainment of adequate dispersion of the CNT within the polymer matrix. Various composite properties, such as electrical resistivity and viscoelastic properties, have been used to assess the state-of-mix and dispersion of the CNT within a base polymer [1, 2].

From a product commercialization perspective the most widely used dispersion processing technology for the production of filled polymer materials is melt compounding. And, of the various types of melt compounding equipment, the twin screw extruder (TSE) dominates the field. So, as expected, much of the dispersion processing for nanocomposite production has focused on melt compounding via twin screw extrusion. Some of the earliest work focused on montmorillonite clay based nanocomposites. These studies focused on the effect of operating conditions [3, 4] as well as process configuration [5]. It was determined that to generate acceptable dispersions that yielded attractive properties it was necessary to strike a balance of the environmental conditions in the compounding process, i.e., shear forces, residence time, and mixing energy input. More recent work that focused on CNT-based composites also considered the influence of operating conditions and process configuration [6-10]. The results of these studies paralleled those of the work on dispersing nanoclays in polymer matrices. An optimum blend of shear forces, residence time and mixing energy needs to be struck to enable the production of high performance nanocomposites.

This paper extends this field of activity and examines the cause-and-effect relationships among the method of compounding, the types of CNT and polycarbonate used, and the composite formulation with the linear and nonlinear viscoelastic properties of the nanocomposites produced.

Experimental

A Leistritz ZSE 18 HP co-rotating, intermeshing twin screw extruder (TSE) equipped with screws 18mm in diameter and 60 L/D in process length was used to melt compound the nanocomposites described in this study. This 12 barrel extruder was configured with K-Tron loss-in-weight feeders at barrel sections #1 (primary feed port) and #5 (downstream feed port using either a top entry port or a side feeder) to dose materials into the melt compounding process. A port for vacuum venting of residual volatiles was provided at barrel #11. Two screw configurations were used. Intensive as well as mild mixing screws were used for primary melt compounding of the nanocomposites. In addition, the mild mixing screw was used for exposing compounded nanocomposites to extended melt residence times under relatively mild extrusion conditions. The process and screw configurations are represented schematically in Figure 1.

CNT-polycarbonate nanocomposites were formulated with three different grades of multi-wall CNT and two different grades of polycarbonate. The identification of these materials and their defining characteristics are articulated in Tables 1 and 2. CNT content was varied between 1 and 7 weight percent. The melt compounding process for the production of the CNT-polycarbonate nanocomposites was varied with respect to screw design (mentioned above) and CNT dosing location (either with the solid resin at barrel #1 or into a fully developed polycarbonate melt at barrel #5). Process conditions for the primary melt compounding operations were maintained at a resin throughput rate of 6.8 kg/hr, a screw speed of 900 rpm and a maximum barrel set temperature of 300°C. Process conditions for exposing the nanocomposites to extended

melt residence times included throughput rates of 2.3 and 6.8 kg/hr, a screw speed of 600 rpm, and a maximum barrel set temperature of 300°C. For most of these extrusion operations the atmosphere at the feed ports was ambient air. However for selected operations a nitrogen "blanket" was maintained at the feeder hoppers and the extruder dosing ports. In all cases the polycarbonate resins were dried at 121°C for a minimum of 4 hours prior to melt compounding.

A TA Instruments ARES G2, equipped with 25 mm diameter oscillating parallel plates, was used to measure the strain amplitude-, frequency- and time-dependent viscoelastic properties of the polycarbonate resins and CNT-polycarbonate compounds. All testing involved a 1.5 minute preheat and a dry nitrogen environment at 235°C. Resin and compound samples were vacuum-dried at 121°C for a minimum of 12 hours, after which they were retained under vacuum at room temperature until consumed for testing. Disk-shaped test specimens were die-cut from 1.6 mm thick sheets prepared by compression-molding the samples between Teflon-coated aluminum foil in a laminating press at 210°C for 15 seconds total and immediately loaded into the parallel plate test fixture.

Strain-dependent viscoelastic properties were measured for shear strain-amplitudes of 0.04 to 400% to define the strain-limit for linear viscoelastic (LVE) behavior. Frequency-dependent LVE properties were measured for a frequency range of 316 to 0.0562 rad/s, requiring approximately 10 minutes to complete, followed by a second, sequential frequency scan from 316 to 0.1 rad/s, requiring approximately 6 minutes to complete. The dual-scan methodology was used to assess thermal stability of the sample. Time-dependent LVE properties were measured at 1 rad/s for a residence time of 23 minutes.

Results and Discussion

CNT Concentration

Figure 2 displays an example of the effect of CNT content on the frequency-dependent complex viscosity of CNT1-PC1 blends. Low-frequency viscosity increases with increasing CNT1 content. High-frequency complex viscosity initially decreases and then increases with increasing CNT1 content. The initial decrease in the high-frequency viscosity is attributed to a slight decrease in molecular weight of polycarbonate PC1 during compounding.

Figure 3 displays the accompanying Cole-Cole plots. This method of presentation for the viscoelastic properties (i.e. loss modulus, G'' , vs. storage modulus, G') "hides" variations in molecular weight but sensitively reveals variations in structure that arise from molecular branching, multiple phase morphology, crystallinity and reinforcing filler-polymer interactions [11]. As shown, the Cole-Cole plot shifts towards higher storage moduli or higher elasticity with increasing CNT1 content, attributable to an increase in CNT-polycarbonate interaction. This is in contrast to the effect of increasing the content of non-interacting filler which would shift the Cole-Cole plot diagonally along the dashed, equal-moduli line.

The change in the LVE properties during the approximately 10 minutes of time between frequency scans is displayed in Figures 4 and 5. The complex viscosity increases (especially at low-frequencies) and the Cole-Cole plots shift towards higher storage modulus, indicating that the CNT-polycarbonate interaction increases during the relatively quiescent (exposure to small cyclic strain) residence time under nitrogen at 235°C. The dynamics of the change in properties needs further study, as will be presented.

CNT Type

The effect of variation in CNT type on the enhancement of complex viscosity and elasticity is shown in Figures 6 and 7. Increases in the levels of CNT1 and CNT3 in polycarbonate PC1 produce similar increases in complex viscosity and structure. However, CNT2 provides enhancements that are nearly equivalent to those produced with the addition of an extra 2% of CNT1 or CNT3. As shown in Table 1, the aspect ratio (length/diameter) of CNT2 is approximately 3 times that of the other two CNT types. Apparently, the differences in aspect ratios are maintained during compounding and provide the differentiation in the CNT-polycarbonate interaction; larger aspect ratios of the CNT produce larger viscosity and elasticity enhancements.

Process Variations

During the course of this study, the effects of the TSE screw configuration (regular, mixing vs. mild, conveying), location of CNT addition (main feed, side feed or top feed) and type of "blanket" gas used on the feed ports (ambient air or dry nitrogen) on the viscoelastic properties were examined. Figures 8, 9 and 10 summarize the results in terms of low-frequency complex viscosity, structural parameter and high-frequency complex viscosity, respectively, as functions of CNT content. The structural parameter is somewhat arbitrarily defined as the storage modulus, corresponding to a constant loss modulus of 2×10^4 Pa. The low-frequency complex modulus and the structural parameter plots reveal similar trends, owing to the feature that both variables have a strong dependence on structure or the magnitude of CNT-polycarbonate interaction. As previously concluded, CNT2 develops higher amounts of CNT-polycarbonate interaction (positive reinforcement) than do CNT1 and CNT3 for all levels of CNT addition.

The compounds that were produced with the addition of the CNT to the main feed port (along with the polycarbonate resin pellets) tend to have lower low frequency complex viscosity and structural parameters than do the compounds produced with addition of the CNT to the top and side feed port (where the polycarbonate is in the melt state). Compounds produced with CNT1 (and presumably, with CNT3, but to be verified) display this trend for all levels of CNT

examined. Compounds produced with CNT2 display this trend only for CNT content of 1.5% and lower. At higher levels of CNT2, the dependence of properties on port of addition is only slight. These features suggest that the addition of the CNT to the main feed port leads to attrition (a decrease in aspect ratio) of the CNT. Additionally, the CNT2 might have a more stable geometry than do the CNT1 and CNT3. Neither the structural parameter nor the low-frequency complex viscosity displays a significant effect of using nitrogen vs. ambient air during the compounding.

The high-frequency complex viscosity data of Figure 10 are impacted by the variation in structure but the relative relationships among the data with respect to method of compounding are different than those observed in Figures 8 and 9. The series of compounds prepared by addition of the CNT to the main feed port with ambient air and the use of a "mild" screw configuration produced the lowest high-frequency viscosity. It is likely that the magnitude of the high-frequency complex viscosity reflects the molecular weight of the polycarbonate, in addition to the amount of CNT-polycarbonate interaction. Specifically, the variation in relative magnitude of the high-frequency viscosity (for any given CNT content) reflects the severity of the compounding process and the accompanying change in the molecular weight of the base PC. This postulate is supported by the results shown in Figures 11 and 12, the complex viscosities and accompanying Cole-Cole plots of polycarbonates PC1 and PC2 and their compounds with 3% CNT1. The difference in the molecular weight of these polycarbonates is readily revealed by the high-frequency complex viscosities of the 3% CNT-polycarbonate compounds. However, the low-frequency complex viscosities and the Cole-Cole plots suggest that the 3% CNT compound containing the lower molecular weight polycarbonate PC2 possess a higher amount of CNT-polycarbonate interaction (perhaps because of increased rates of diffusion of the lower molecular weight polycarbonate). Note that the difference in molecular weight is "hidden" in the Cole-Cole plot.

Residence Time

It has been shown that the effect of quiescent residence time at 235°C in an inert environment is to increase CNT-polycarbonate compound viscosity and CNT-polycarbonate interaction. This might indicate that the inter-diffusion of the CNT with the polycarbonate has not attained completion during the compounding processes examined. An attempt was made to increase the residence time during compounding by using multiple passes of the 3% CNT-polycarbonate compounds through the TSE equipped with the "mild" screw configuration. Feed rates of 2.3 and 6.8 kg/hr were used with a screw speed of 600 rpm. Compounds containing 3% CNT in polycarbonate PC1 were subjected to three passes. An example of the significant changes in frequency-dependent complex viscosity for the CNT1-PC1 sample is shown in Figure 13. Viscosity of the compound decreases, especially at high frequencies, with increasing number of passes in the TSE.

Preliminary studies of TSE residence times, using small quantities of color concentrates with the polycarbonate PC1, indicate that the mode of the residence time distribution for this resin was approximately 30 s for the 6.8 kg/hr rate and 60 s for the 2.3 kg/hr rate. However, Figure 13 suggests that an equivalent shear history was attained for the samples exposed to the 3 passes at 6.8 kg/hr and to the 2 passes at 2.3 kg/hr. Although the frequency-dependent viscosity of the 3% CNT-polycarbonate compound is significantly different from that of the base polycarbonate (a feature that likely affects TSE residence time) it is assumed that the residence time for the compound was 30 s for a feed rate of 6.8 kg/hr which translates to 45 s for a feed rate of 2.3 kg/hr. Figures 14 and 15 show the effect of residence time within the TSE, equipped with the mild screw configuration, on the structural parameter and high frequency complex viscosity, respectively. For each of the three CNT types, the 3% CNT-polycarbonate undergoes an apparent decrease in structure, attainment of a minimum then an increase with increasing TSE residence time. These changes are accompanied by a continuous decrease in polycarbonate molecular weight, likely caused by chain-scission. The formation of CNT-polycarbonate interaction might act as a shear stress concentrator or intensifier that enhances the rate of chain scission. This postulate further suggests that the higher negative slopes of the high-frequency viscosity vs. residence time for the CNT2 and CNT3 containing compounds reflects a stronger CNT-polycarbonate interaction than is the case for CNT1-PC1. This is in contrast to the very slight change in viscosity that occurs with residence time for polycarbonate PC1 in the presence of air or nitrogen blankets at the entry ports. The increase in the structural parameter that is measured during the second frequency-scan, relative to the magnitude measured during the first frequency scan indicates that the significant reduction in CNT-polycarbonate interaction (caused by the multiple passes within the shear environment provided by the "mild" screw configuration) can reform if provided a quiescent (low strain) recovery time. However, the high-frequency viscosity reduction during multiple passes does not significantly recover during the two frequency scans. The creation of lower molecular weight polycarbonate species and the accompanying enhancement of diffusion into the CNT could be the cause of the formation of the minima observed in the structural parameter vs. TSE residence time data, Figure 14.

Viscoelastic Property Considerations

The viscoelastic properties discussed thus far have been LVE properties. Figures 16 and 17 display typical changes in complex viscosity and loss tangent as functions of shear strain amplitude, CNT content and CNT type. Departure from zero indicates the strain-limit for LVE behavior for a given compound at an angular frequency of 1 rad/s. Figure 18 shows that the LVE strain-limit for complex viscosity at an angular frequency of 1 rad/s decreases with increasing CNT content. CNT2-containing compounds display lower LVE strain-limits than do the compounds containing the other two CNTs. These trends suggest that the LVE strain-limit depends upon the amount or strength of CNT-polycarbonate interaction. Support for this postulate is provided by the correlation between the LVE strain-limit and low frequency complex viscosity, shown in Figure 19, where CNT type and content become "hidden", i.e. all the data collapse onto a single curve. Although the trends for the LVE strain-limit of the loss tangent are similar to those shown for the complex viscosity LVE strain-limit,

the loss tangent is more sensitive to strain than is the complex viscosity. Figure 20 reveals that LVE departure begins at lower strains for the loss tangent than it does for the complex viscosity. The features associated with LVE strain-limits indicate complex behavior of CNT polycarbonate compounds and the need to define and use experimental protocols that produce LVE responses.

Conclusions

The frequency-dependent viscoelastic properties of CNT-polycarbonate composites reveal that CNT provides positive reinforcement of polycarbonate through the formation of CNT-polycarbonate interaction. The CNT polycarbonate interaction increases with increasing CNT content and with increasing CNT aspect ratio. The amount of CNT-polycarbonate interaction is also influenced by the method of compounding. The addition of the CNT with the polycarbonate pellets appears to cause CNT attrition (perhaps by a decrease in the CNT aspect ratio). Addition of the CNT to a TSE at ports after a melt is attained provides higher CNT-polycarbonate interaction. An increase in TSE residence time (through the use of multiple passes) decreases the high-frequency complex viscosity of CNT-polycarbonate compounds. This feature is attributed to a decrease in polycarbonate molecular weight via a chain-scission process that is intensified by the presence of the CNT-polycarbonate interaction.

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Acknowledgements

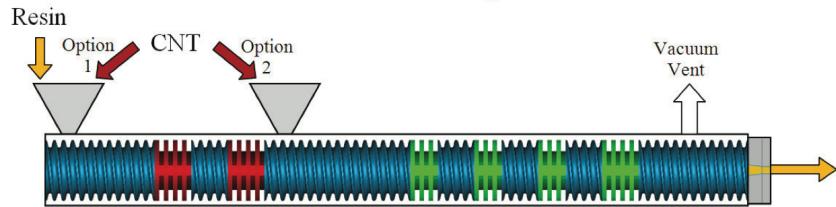
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ID	Producer	Grade	Type	Mean Diameter (nm)	Aspect Ratio	Purity
CNT1	CNano	FloTube™9000-H	Multi-walled	10.9	119	96.2%
CNT2	SouthWest Nano Technologies	SMW™-200X	Specialty Multi-walled	10	420	98.5%
CNT3	SouthWest Nano Technologies	SMW™-100	Specialty Multi-walled	9	144	98.9%

Table 1. Description of CNT Materials

ID	Producer	Grade	Melt Mass-Flow Rate (g/10 min)	Melt Volume-Flow Rate (in³/10 min)	Zero Shear Rate Viscosity (Pa·s) at 235°C
PC1	SABIC Innovative Plastics	Lexan IR2240	11 (300°C/1.2 kg)	0.580 (300°C/1.2 kg)	5970
PC2	SABIC Innovative Plastics	Lexan OQ1022	11 (250°C/1.2 kg)	0.647 (250°C/1.2 kg)	940

Table 2. Description of PC Materials



Mild Screw Configuration

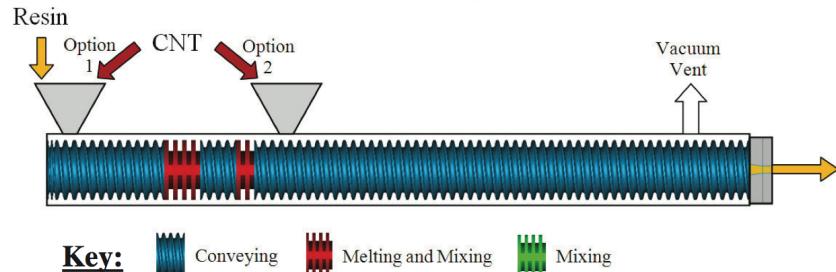


Figure 1. Schematic representation of the process configurations and screw designs.

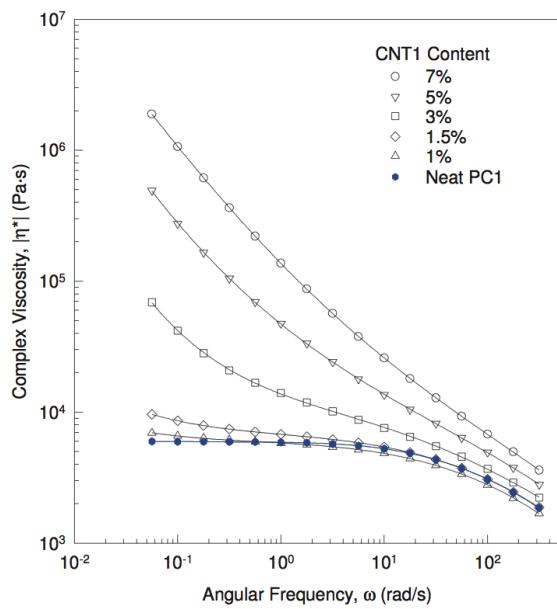


Figure 2. Complex Viscosity of CNT1-PC1 with CNT Addition at Main Feed, Intensive TSE Screw

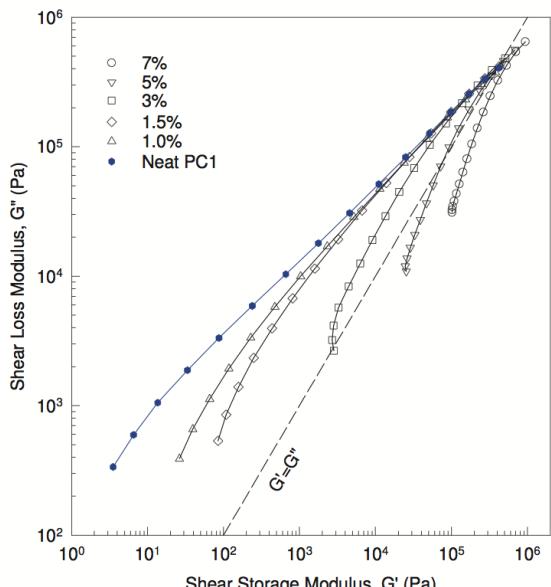


Figure 3. Cole-Cole Plots of CNT1-PC1 with CNT Addition at Main Feed, Intensive TSE Screw

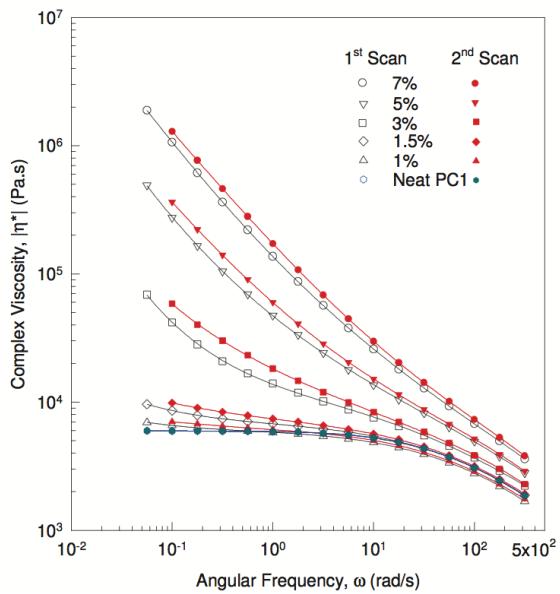


Figure 4. Change in Viscosity of CNT1-PC1 Compounds Between Frequency-Scans, CNT Addition at Main Feed, Intensive TSE Screw

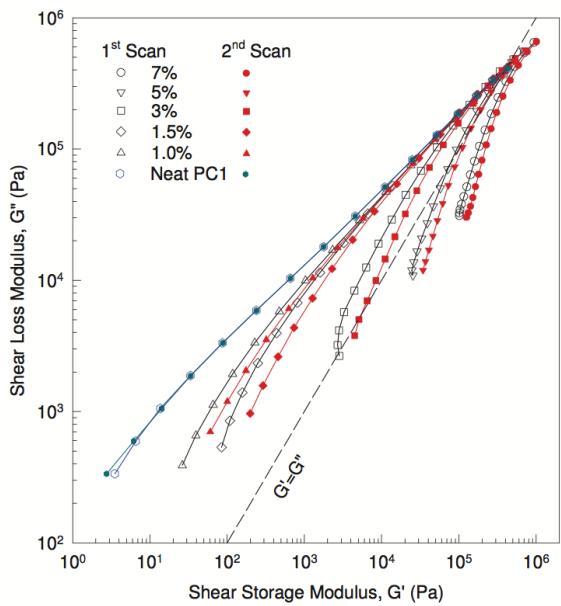


Figure 5. Change in Cole-Cole Plots of CNT1-PC1 Compounds Between Frequency-Scans, CNT Addition at Main Feed, Intensive TSE Screw

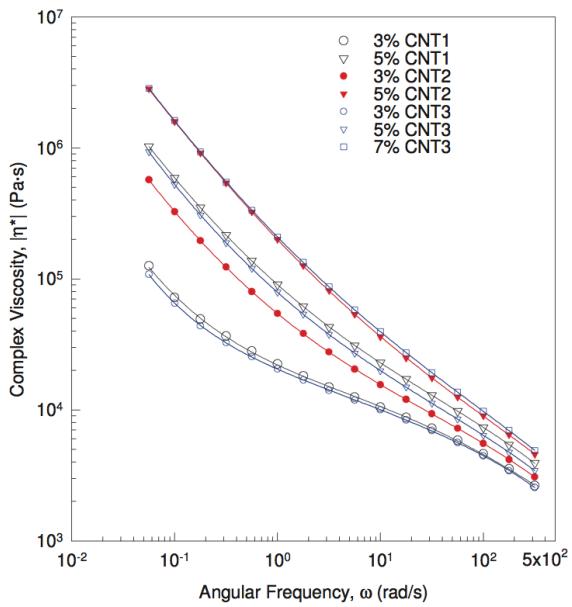


Figure 6. Effect of CNT-Type on the Complex Viscosity of CNT-PC1, Top Feed, Intensive TSE Screw

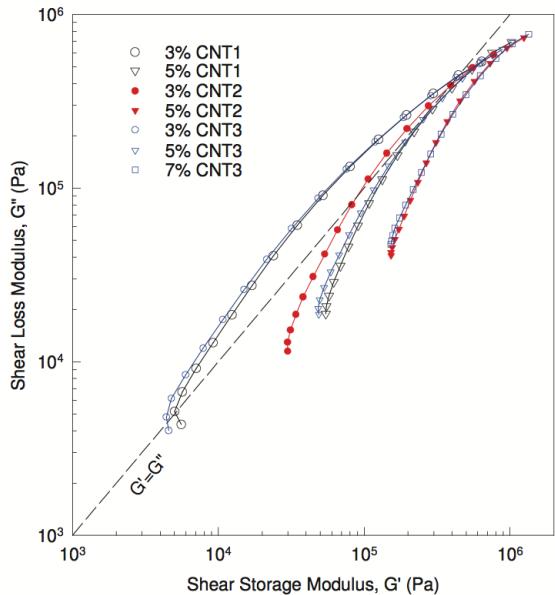


Figure 7. Effect of CNT-Type on the Cole-Cole Plots of CNT-PC1, Top Feed, Intensive TSE Screw

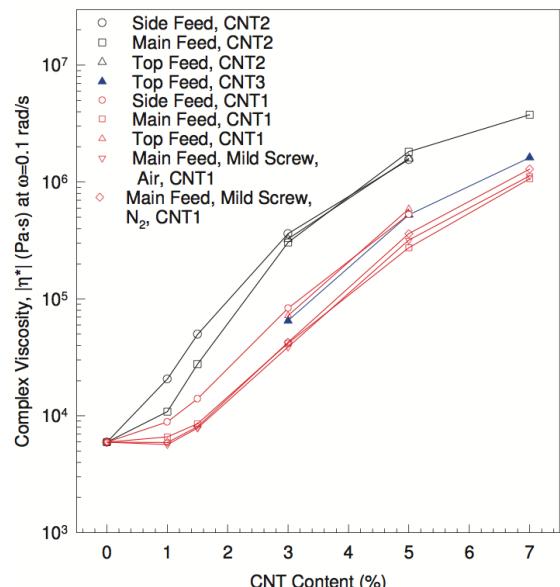


Figure 8. Low-Frequency Complex Viscosity of CNT-PC1 Compounds at 235°C

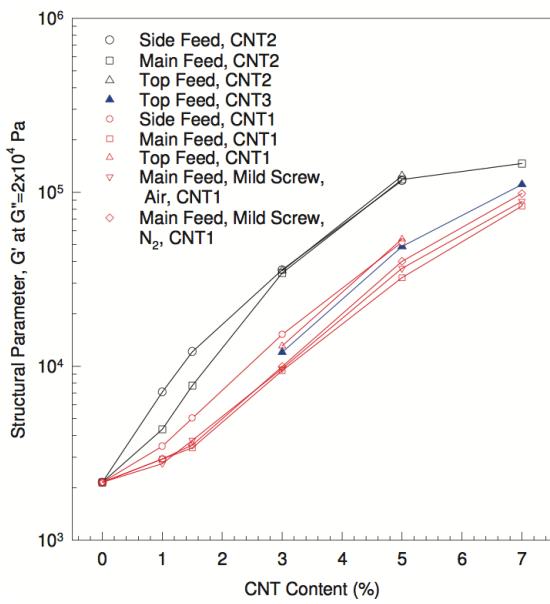


Figure 9. Structural Parameter of CNT-PC1 Compounds at 235°C

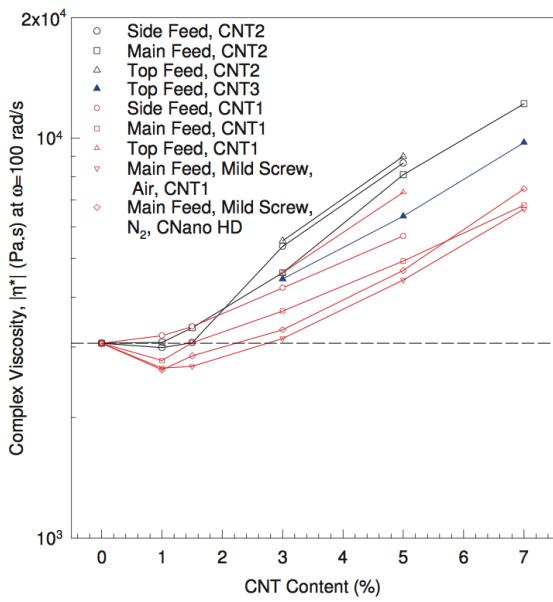


Figure 10. High-Frequency Complex Viscosity of CNT- PC1 Compounds at 235°C

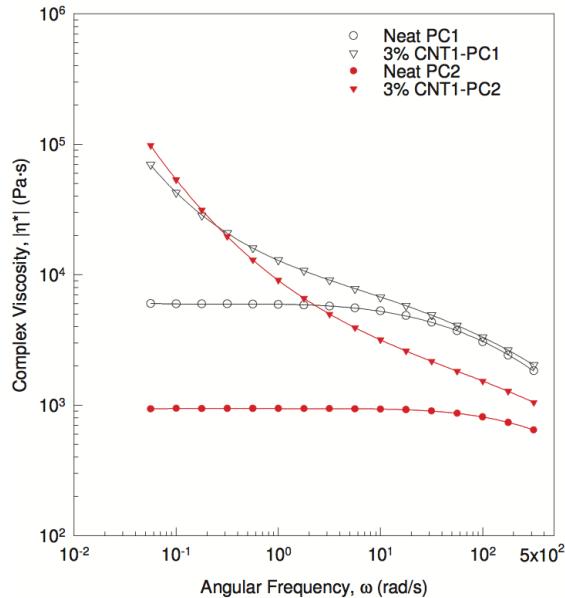


Figure 11. Effect of PC-Type on Complex Viscosity of 3% CNT1-PC Compounds at 235°C, Main Feed, Mild Screw, N2

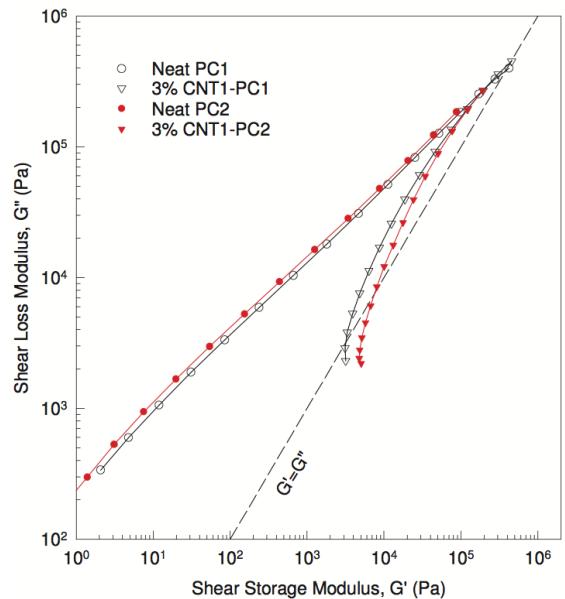


Figure 12. Effect of PC-Type on Cole-Cole Plots of 3% CNT1-PC Compounds at 235°C, Main Feed, Mild Screw, N2

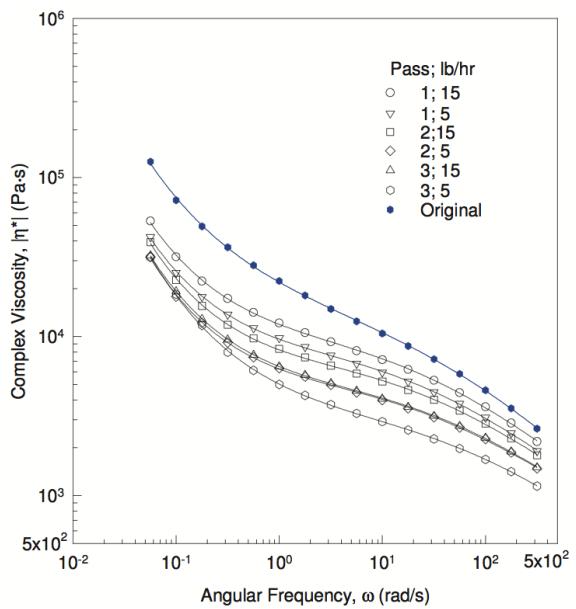


Figure 13. Effect of Residence Time in TSE on Complex Viscosity of 3% CNT1-PC1, Mild Screw, Vac/Air

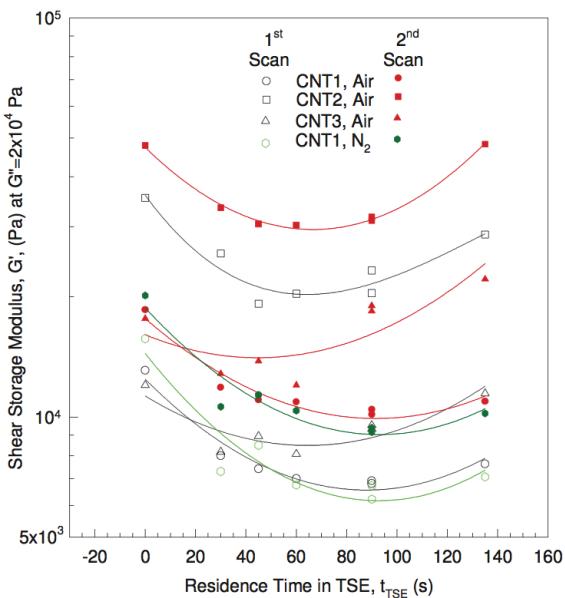


Figure 14. Effect of Residence Time in TSE on the Structural Parameter of 3% CNT-PC1 Measured During the First and Second Frequency-Scans at 235°C

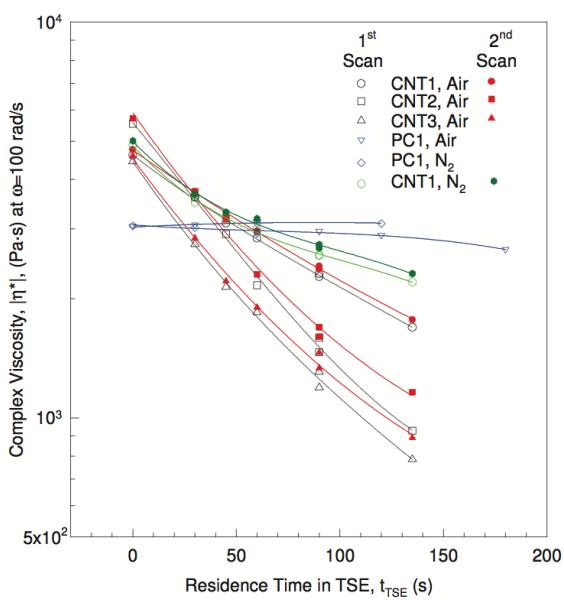


Figure 15. Effect of Residence Time in TSE on Frequency Complex Viscosity of 3% CNT-PC1 the High- Measured During the First and Second Frequency-Scans at 235°C

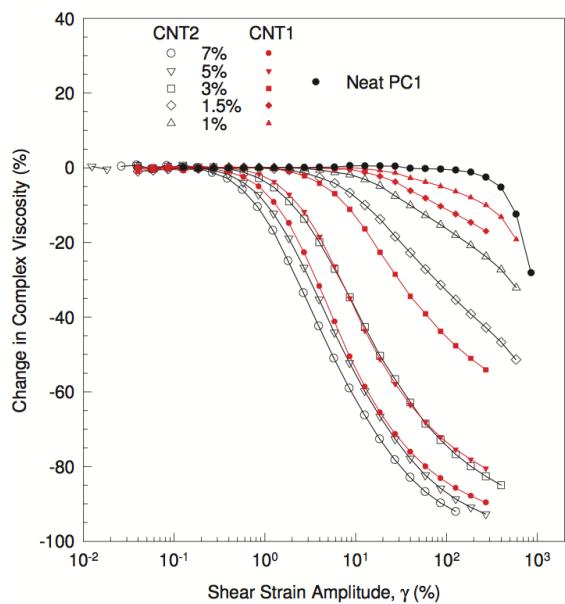


Figure 16. Percent Decrease in Complex Viscosity of CNT-PC1 Compounds as Functions of Shear Strain Amplitude and CNT Content at 235°C and $\omega=1$ rad/s

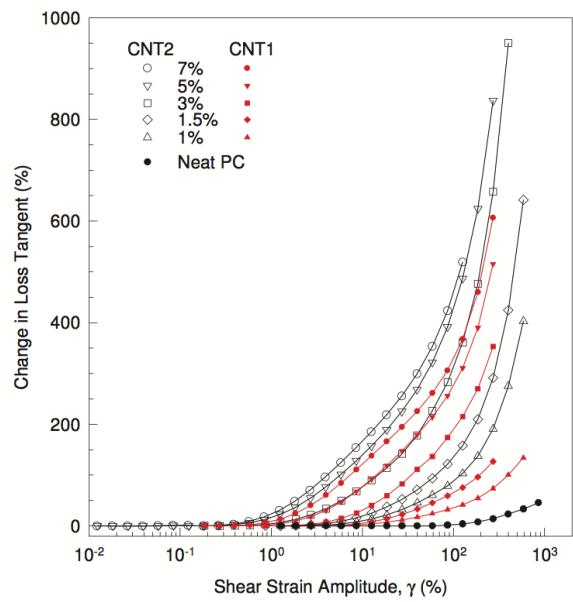


Figure 17. Percent Increase in Loss Tangent of CNT-PC1 Compounds as Functions of Shear Strain Amplitude and CNT Content at 235°C and $\omega=1$ rad/s

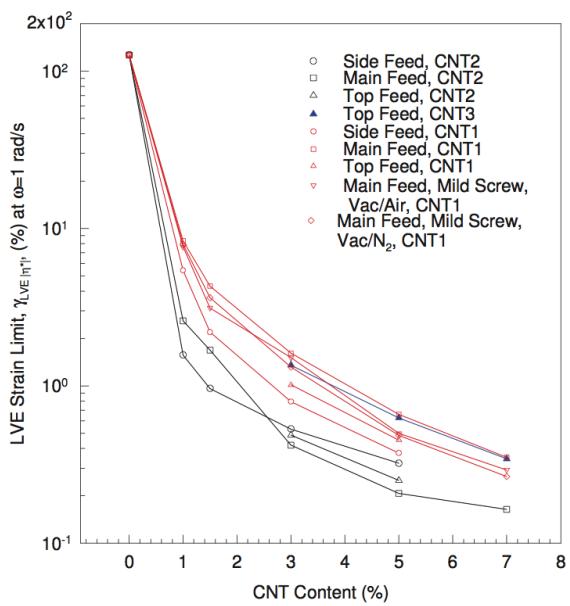


Figure 18. LVE Strain Limit for Complex Viscosity of CNT-PC1 Compounds at 235°C and $\omega=1$ rad/s

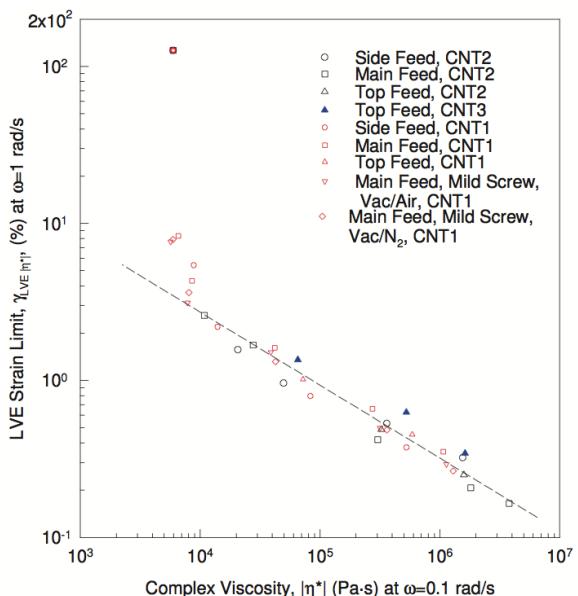


Figure 19. Correlation Between LVE Strain-Limit and Complex Viscosity for CNT-PC1 Compounds at 235°C and $\omega=1$ rad/s

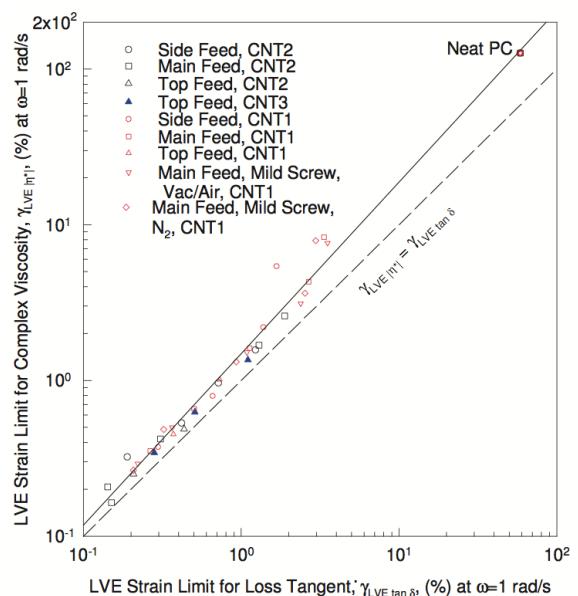


Figure 20. Relationship Between LVE Strain-Limits for Complex Viscosity and Loss Tangent for CNT-PC1 Compounds at

235°C and $\omega=1$ rad/s

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