Accelerating TTS Experiments Using Frequency Chirps

Keywords: TTS, Polymer, Chirp, OWCh

RH156

ABSTRACT

Frequency chirps generate moduli and phase angles from a broad range of frequencies in a short period of time. Recent work has minimized spectral leakage in strain [1] and stress-based [2] chirps, enabling fast frequency data collection on both separate motor/transducer and combined motor/transducer instruments such as the ARES™ System platform and HR series instruments. This note will describe using chirps to accelerate Time-Temperature Superposition (TTS) data on the HR series instruments using Polystyrene and Polycarbonate as examples.

INTRODUCTION

Time-temperature superposition is used to determine the mechanical properties of polymers using the relationship between the relaxation of polymers, their mechanical properties, and the temperature of the measurement. Frequency chirps can be used to accelerate data acquisition, shortening measurements from hours to less than an hour in ideal cases and otherwise offering significant time savings in addition to higher data density.

A traditional TTS experiment uses frequency sweeps done isothermally and increments temperature over a range of interest. The measurements are then shifted by a shift factor α_T that multiplies the frequency axis. Some measurements benefit from shifting the moduli (y axis) to account for density changes. A significant overlap of the data is required to successfully determine the shift factor. Once collected, these shift factors can be fit to models such as the WLF and Arrhenius, depending on the temperature range.

A frequency chirp experiment can be used to complete an isothermal frequency sweep in a fraction of the time while maintaining the same isothermal conditions. The time savings for a chirp relative to a frequency sweep can be realized in three ways: less time for the same frequency range, same time for a wider frequency range and less temperature steps, or ramping temperature while chirping to save time on equilibration. These methods can be optimized for the size of the shift factors, e.g. a chirp ramp from the glassy state to rubbery plateau is more efficient than long chirps while long chirps in wide temperature steps are more efficient in the rubbery plateau into the molten state of a polymer.

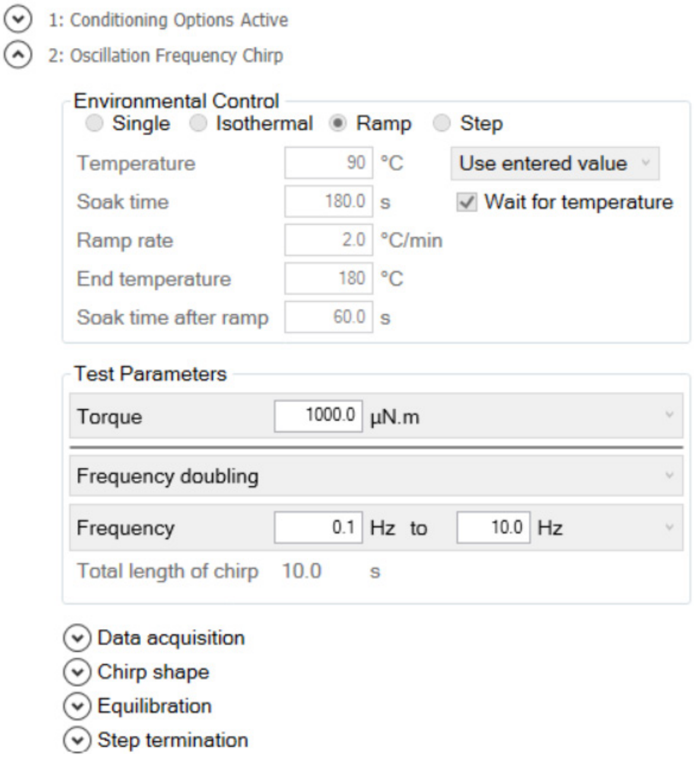
These strategies of acceleration for TTS experiments with chirps can also be mixed, utilizing a short chirp for ramps in the glass transition region and then long chirps where the shift factors are lower.

EXPERIMENTAL

A TA Instruments™ Discovery™ HR 30 Rheometer was used for all experiments. Temperature ramps and steps from glass transition to the molten region were done with an 8 mm plate for polystyrene (PS) and polycarbonate (PC) samples.

Frequency chirp ramps and temperature steps can be done with the same step in TRIOS™ Software based on the mode selection. An example of the ramp is shown in Figure 1. Axial force and auto-strain can be set in the conditioning options step. A target axial force of 0 N, minimum torque of 10 µNm, and maximum strain of 10% was set for these experiments.

A torque or stress-based chirp is used because the experiment starts in the stiff glassy region where stress/torque chirps typically offer better performance. An initial amplitude of 1000 µNm was used. A zero-torque equilibration is performed between each chirp.



1: Conditioning Options Active

2: Oscillation Frequency Chirp

Environmental Control

○ Single ○ Isothermal ● Ramp ○ Step

Temperature 90 °C Use entered value

Soak time 180.0 s ☑ Wait for temperature

Ramp rate 2.0 °C/min

End temperature 180 °C

Soak time after ramp 60.0 s

Test Parameters

Torque 1000.0 µN.m

Frequency doubling

Frequency 0.1 Hz to 10.0 Hz

Total length of chirp 10.0 s

Figure 1. Frequency Chirp ramp experimental setup. A conditioning options step is included before the chirp for axial force control and auto-strain.

This equilibration gives time for the material to relax between chirps and adjust the gap to maintain 0 axial force. These parameters can be adjusted in the equilibration drop-down of the step.

The Frequency Chirp ramp can be followed by a much longer isothermal chirp (Figure 2) by selecting the *Single* radial button for a single chirp or the *Step* radial button for a set of chirps at pre-determined temperature increments.

The shift factors for TTS between the glass and molten states of a polymer typically follow a WLF form and are much higher in the glass transition region and rubbery plateau than near the melt region. The WLF fit equation used is below [3]:

$$\log \alpha_T = \frac{-C_1\,(T-T_{ref})}{C_2 + (T-T_{ref})}$$

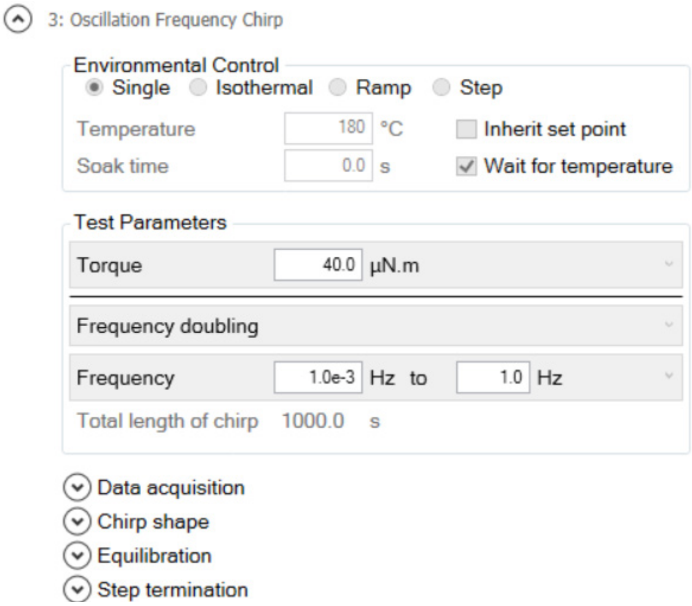
where:

α_T is the shift factor

C_1 and C_2 are fitting constants

T is temperature and

T_{ref} is the reference temperature



3: Oscillation Frequency Chirp

Environmental Control

● Single ○ Isothermal ○ Ramp ○ Step

Temperature 180 °C ☐ Inherit set point

Soak time 0.0 s ☑ Wait for temperature

Test Parameters

Torque 40.0 µN.m

Frequency doubling

Frequency 1.0e-3 Hz to 1.0 Hz

Total length of chirp 1000.0 s

Data acquisition

Chirp shape

Equilibration

Step termination

Figure 2. Single Frequency Chirp performed after the ramp. A single chirp or series of chirps at set temperature increments can be used.

Using a short chirp while ramping is more effective at lower temperatures in the glass transition where the shift factor is large and changing quickly. Large shift factors mean that data needs to be collected close together in temperature. A stepped experiment would require many small steps with equilibration for each while a ramped chirp experiment collects data quickly and frequently. A longer chirp or set of longer chirps with much higher temperature spacing is more efficient than ramping when approaching the melt region because the shift is much smaller.

RESULTS AND DISCUSSION

The method described in Figure 1 produces a little less than one frequency chirp every 1 °C when accounting for the chirp duration, baseline, and equilibration between chirps. This chirp produces frequency content from 0.1 to 10 Hz. A select few chirps are shown in Figure 3 for each of the key regions of a thermoplastic: near the glass state (100 °C), the transitions state (110 °C, 125 °C), the rubbery plateau (150-170 °C), and the final longer chirp for the molten region (180 °C).

All of the chirps in the experiment, including the select examples in Figure 3, can be shifted automatically in TRIOS Software to produce the curve in Figure 4 along with a similar experiment performed using discrete frequency sweeps (DFS) for comparison. The frequency sweeps take much longer than a chirp and require several more temperature steps above 180 to acquire data to shift into the same frequency range as the chirp data. The high temperatures and long times result in degradation of the polymer as seen where the frequency sweep data deviates from the chirp at the lowest frequencies.

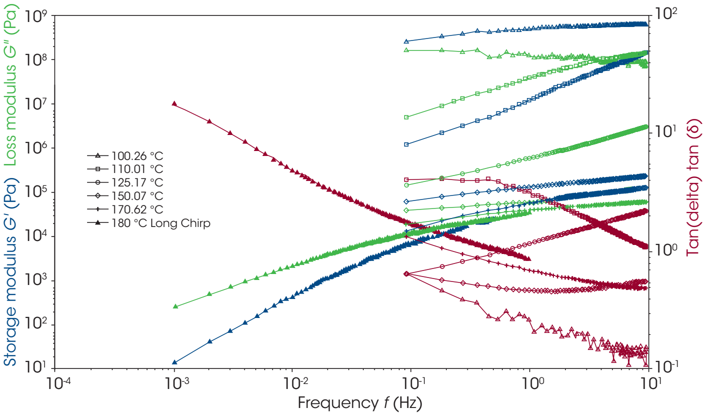


Figure 3. Select chirps from a polystyrene ramped chirp experiment that terminates in a long isothermal chirp at 180 °C

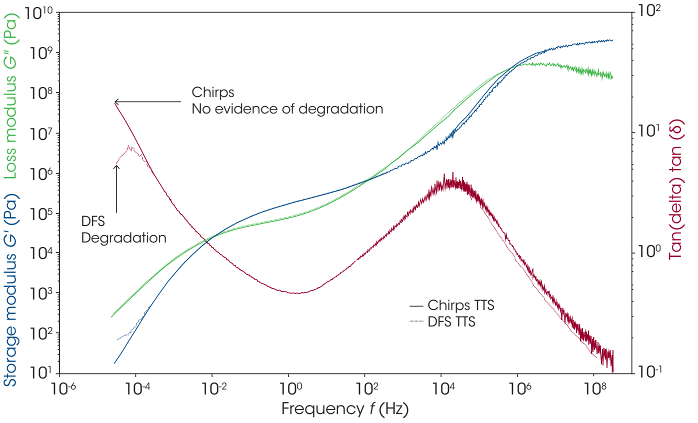


Figure 4. Shifted data for polystyrene from a combined chirp ramp and isothermal long chirp compared to data from a discrete frequency sweep (DFS). The reference temperature was 150 °C. The chirp shows little to no evidence of degradation because a long low frequency chirp was used at 180 °C instead of several time consuming DFS sweeps between 180 and 260 °C that were required for the frequency sweeps.

Until the degradation at higher temperatures, the DFS and chirp data are in very good agreement. The overall experimental duration for the chirp is ~3,500 s (< 1h) where the frequency sweep data in this setup take ~13,700 s or nearly four hours. These discrete frequency sweeps were collected using isothermal frequency sweeps with 5-minute temperature soaks at 5 °C increments between 100 and 180 °C, then using 20 °C increments up to 260 °C. The chirp method also provides significantly more data points to produce reliable shifts. The chirp method near the extremes of stiffness (very low and very high) can be noisier as chirps don't utilize multiple isothermal cycles as a discrete frequency sweep does, but data between the extremes is nearly identical.

The resulting shift factors for the frequency sweep and chirp can also be compared and are shown in Figure 5. These data show how the shift factor changes graphically. Note that the plot is semi-logarithmic and the shift factors go from 10,000,000 to less than 1 from near the glassy state to the molten region (100 °C to 180 °C). The shift factor at the reference temperature is, by definition, 1 and near perfect agreement is observed between the traditional DFS experiment and the ramped chirp close to the reference. At the coldest temperatures away from the reference there is a slight deviation between the two data sets owing to small differences in the data that accumulate further away from the reference that data is taken. More data typically results in less error with these shifts so it is likely that the chirp ramp data can be considered more reliable due to having much more overlap with chirps very closely spaced in temperature. The WLF fit also shows good agreement between C_1 and C_2 for the chirp rampa and DFS temp sweep.

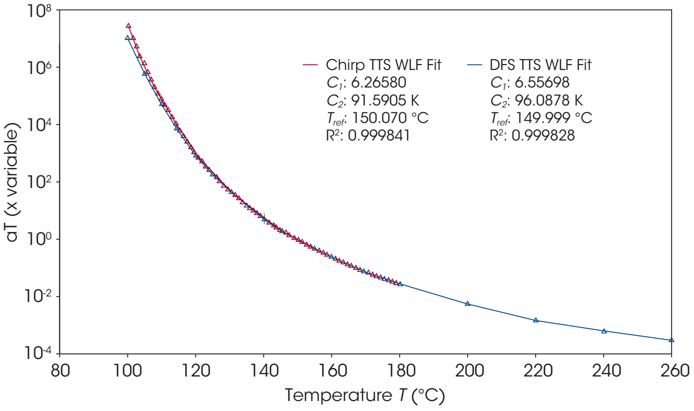


Figure 5. Shift factors for polystyrene with DFS (blue) and Chirp data (red). The WLF fitting was performed from 100 to 180 °C in TRIOS Software with the color-coded fit results displayed showing good agreement.

The chirp ramp followed by long isothermal chirps can be applied to a polycarbonate sample as well with similar results. Figure 6 and the shift factor comparison in Figure 7 show the comparison between the DFS and Chirp ramp with a long isothermal chirp. The chirp ramp portion takes around 2,000 s followed by a 1,000 s chirp at 220 °C for another roughly 3,000 s experiment, while the DFS TTS swept from 150 °C to 200 °C in 5 °C increments, then 20 °C increments up to 260 °C takes about 10,000 s. Thermal degradation was not evident in this sample. Good agreement is observed for the curve as well as the shift factors and only small deviations far away from the reference temperature are observed. The WLF fits also show good agreement between the determined C_1 and C_2.

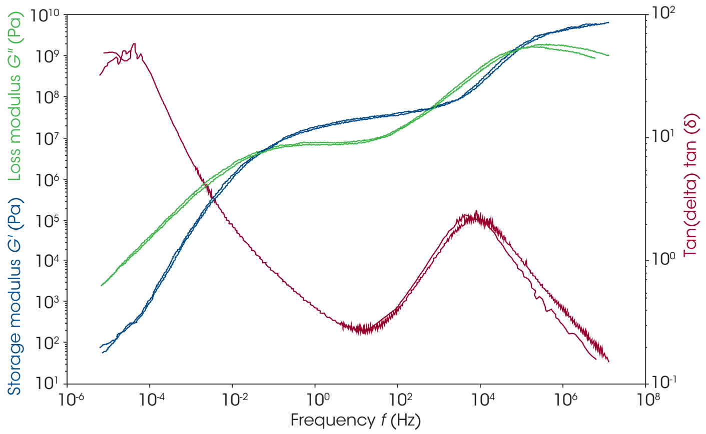


Figure 6. Polycarbonate Chirp TTS vs DFS TTS with reference temperature of 180 degrees

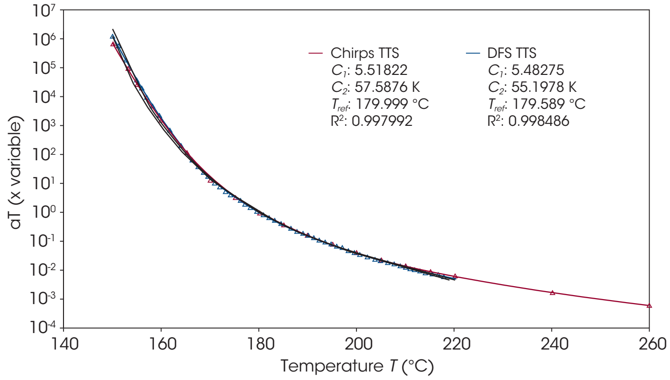


Figure 7. Shift factors for polycarbonate with DFS (blue) and Chirp data (red). The WLF fitting was performed from 150 to 240 °C in TRIOS with the color-coded fit results displayed showing good agreement.

CONCLUSIONS

Frequency chirps utilizing a combination of temperature ramps and long chirps were compared to a more traditional discrete frequency sweep temperature step protocol. The data produced by the frequency chirp was in very good agreement with the discrete frequency sweep while taking only a fraction of the time and providing more data that can increase the quality of TTS shifting. This note demonstrated strategies to accelerate data acquisition by ramping where shift factors are typically high near the glassy region and using long isothermal chirps where the shift factors are small as in the molten region.

REFERENCES

1. Geri, M., et al., Phys. Rev. X 8, 041042, 2018
2. Hudson-Kershaw, R. et al., M., J. Non-Newton. Fluid Mech, 333, 105307, 2024
3. Williams, M., et al. J. Am. Chem. Soc., 77, 3701, 1955

ACKNOWLEDGMENTS

For more information or to request a product quote, please visit www.tainstruments.com to locate your local sales office information.

This paper was written by Kevin Whitcomb Ph.D., Principal Application Scientist at TA Instruments.