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Title: Time-Temperature Superposition Applied to Low Estane Molecular Weight PBX 9501

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Time-Temperature Superposition Applied to Low Estane Molecular Weight PBX 9501
Darla Graff Thompson, 15 November 2011
Data Report for Enhanced Surveillance, C8

These slides provide a data summary of many years of ESC work and at least several different studies and reports. The overall subject is the mechanical properties characterization of PBX 9501 and the change of those properties as Estane molecular weight (Mw) is reduced. An analytical tool that has proven very useful is the application of time-temperature superposition principles to mechanical response, directly relating the effects of temperature and strain rate on the mechanical response of PBX composites.

"Virtual Aging Study" – ca. 1999-2001; Estane was hydrolyzed (70°C, 74%RH) to FOUR different molecular weights (115, 88, 72 and 45 kD) and then used to formulate PBX 9501 which was then mechanically characterized using quasi-static tension and compression at three temperatures (-15, 23 and 50°C) and at two crosshead speeds (1 and 10in/min in tension and 0.5 and 5 in/min in compression).

"Massive Aging Study"- ca. 2003-2005; PBX 9501 was pressed, and cores were hydrolyzed (70°C, 74%RH) to FIVE different molecular weights (21, 7, 4.1, 3, 2.6 kD); specimens were machined from these cores for mechanical characterization using quasi-static tension and compression at three temperatures (-15, 23 and 50°C) and at two crosshead speeds (1 and 10in/min in tension and 0.5 and 5 in/min in compression), to match the conditions of the "Virtual Aging Study."

"Universal Hemi Baseline PBX 9501 Mechanical Characterization" – ca. 2009; Using Pantex-pressed PBX 9501 Universal Hemis, quasi-static uniaxial tension and compression tests were performed at 5 temperatures and 5 rates, all using strain rate control, to provide a high-quality PBX 9501 mechanical baseline.

"Time-Temperature Superposition Applied to Baseline PBX 9501 and 9502" – ca. 2010; Time-temperature analysis of plastic-bonded explosives PBX 9501 and PBX 9502 in tension and compression, D G Thompson, R DeLuca, G W Brown, and W J Wright, manuscript accepted by Journal of Energetic Materials, 2011.

"Time-Temperature Superposition Applied to Five PBX Composites" (Funded in part by Joint Munitions) – ca. 2011, LA-UR 11-04059, "Time-Temperature Superposition Applied to PBX Mechanical Properties," Proceedings of the APS Shock Compression of Condensed Matter, Chicago IL, 26 June – 01 July 2011.

"Time-Temperature Superposition Applied to Reduced Estane Mw PBX 9501 from the Virtual and Massively-Aged Studies" – ca. 2011, Results documented in these slides.

Abstract

PBX 9501 is 95 weight% (wt%) HMX, 2.5 wt% Estane (a polyester-polyurethane), and 2.5 wt% plasticizer. Under hydrolytic conditions, Estane has been shown to hydrolyze or cleave in its polyester segment, reducing the molecular weight of its polymer chains. In such a polymer, reduced chain length leads to lower cross-linking associated with lower modulus and strength. Two accelerated aging studies were performed (70°C and 74%RH) to examine the effect of Estane hydrolysis (reduction of molecular weight) on PBX 9501. The "virtual" aging study hydrolyzed Estane alone, and then formulated PBX 9501 with the reduced Mw Estane. Later, the "massively-aged" study formulated and pressed PBX 9501 and exposed this material to hydrolytic conditions to reduce the Estane Mw. Together the two studies spanned the full range of Estane Mw. In both studies, SIX experimental conditions were measured in tension and compression, spanning three temperatures and two strain rates. There has been some criticism of these test data because they were measured using crosshead control on the Instron and because there was some difficulty in machining somne of the low Estane Mw specimens with the desired high tolerances. In separate work, we performed high-quality tension and compression tests using strain rate control on baseline PBX 9501, and we showed that a very simple time-temperature analysis could be used to form master curves which spanned ~10 orders of magnitude of strain rate and could be reasonably shifted to a broad range of temperatures. Using the same shift factors as were established for the high-quality baseline PBX 9501 data, <u>we here show the results of applying time-temperature superposition to the historic data sets from the accelerated aged studies</u>. Importantly, we show that for crosshead controlled tests, the actual strain rate at the specimen can be calculated and approximated (averaged), and that by doing so, the master curves for crosshead controlled and strain rate controlled tests are nearly identical. In the end, in both tension and compression, we put forth a series of master curves, one for each Estane Mw studied. Together, the master curves show a consistent evolution as Estane Mw is decreased, giving confidence that the accelerated aging data do capture the real material response and providing a useful description of that behavior for modeling. In addition, the premise of time-temperature superposition gives confidence that material response can be interpolated between points, or slightly extrapolated, to understand mechanical behavior at conditions not directly measured.

PBX 9501 Universal Hemisphere Baseline Compression

These plots indicate the three stress-strain parameters used to characterize mechanical response and carried forward in the time-temperature analysis.

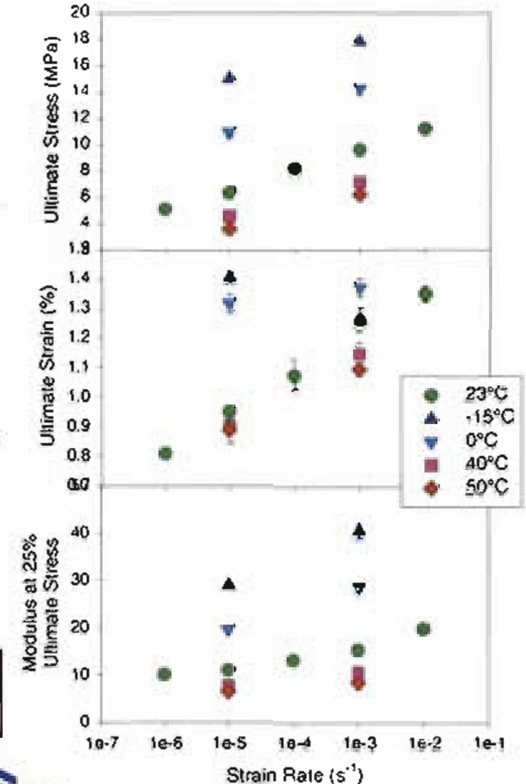
Temperature dependence, at two rates;

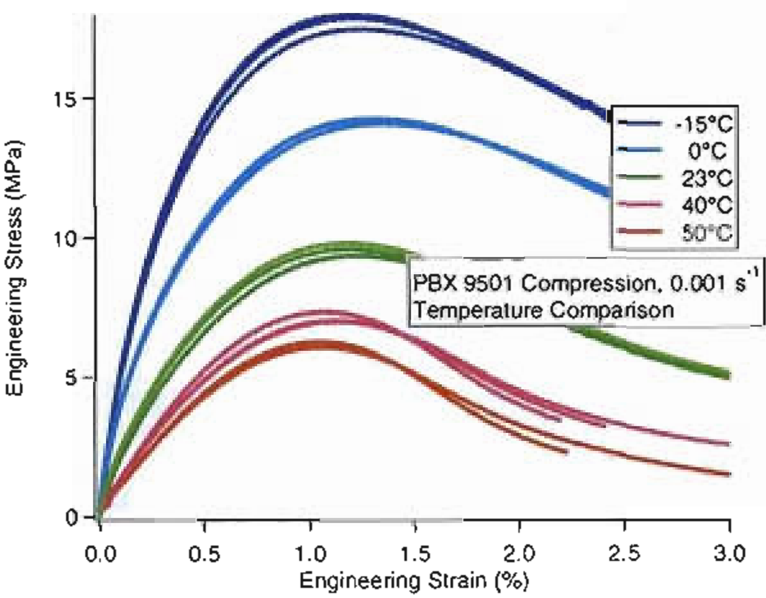
stress-strain parameters

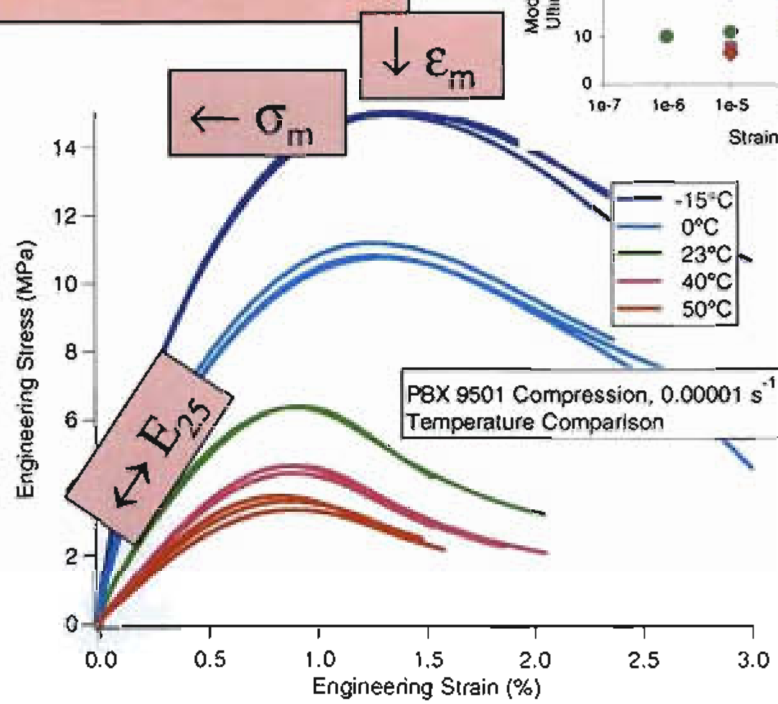
σ_m = ultimate stress

ε_m = ultimate strain

E_{25} = modulus (slope)







Background/History
Time-Temperature Superposition Analysis

We have used the simple Siviour relation (below) for our Time-Temperature analyses, attracted by its simplicity (one parameter, A) and its apparent success with EDC 37 compressive strength (see Williamson reference).

- **Glasstone, Laidler, Eyring (Theory of Rate Processes, 1941)** →

$$\log a_T = \log\left(\frac{v_1}{v_2}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- **Williams, Landel & Ferry (1955)** →

$$\log a_T = \log\left(\frac{\eta}{\eta_{Ts}}\right) = \frac{-C_1(T - T_S)}{C_2 + (T - T_S)}$$

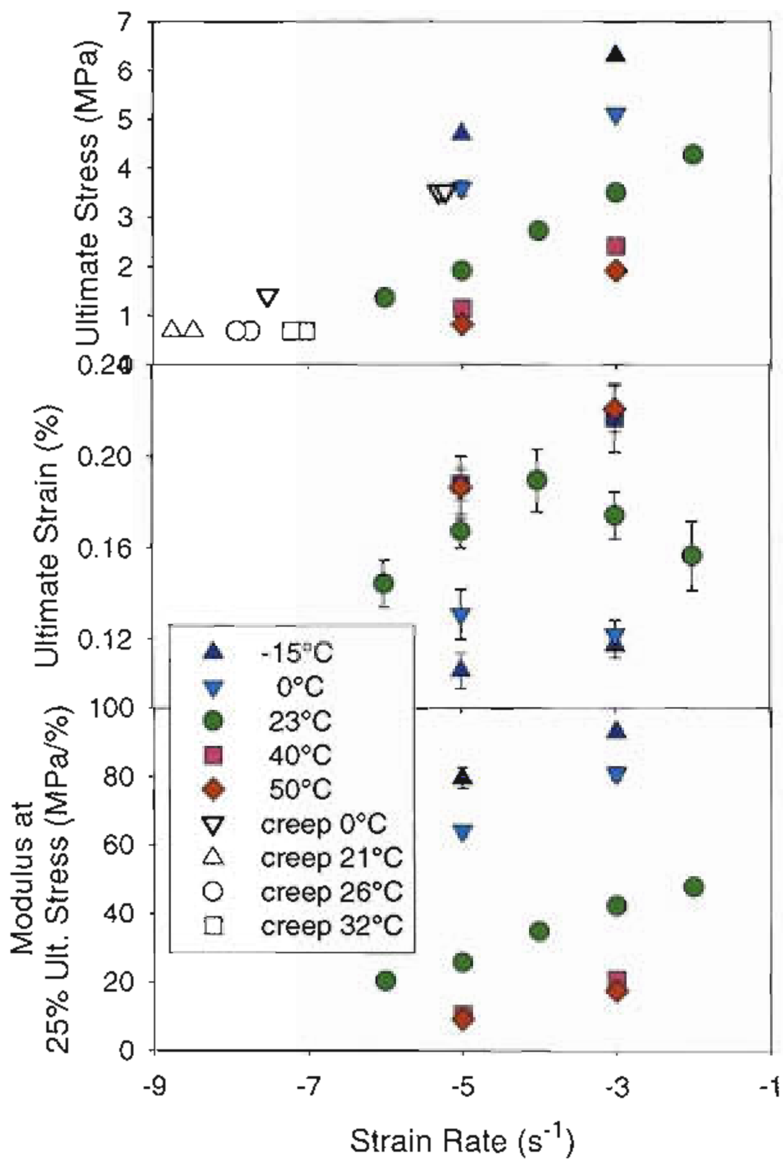
- **Siviour, Walley, Proud, Field (Polymer 2005)** →

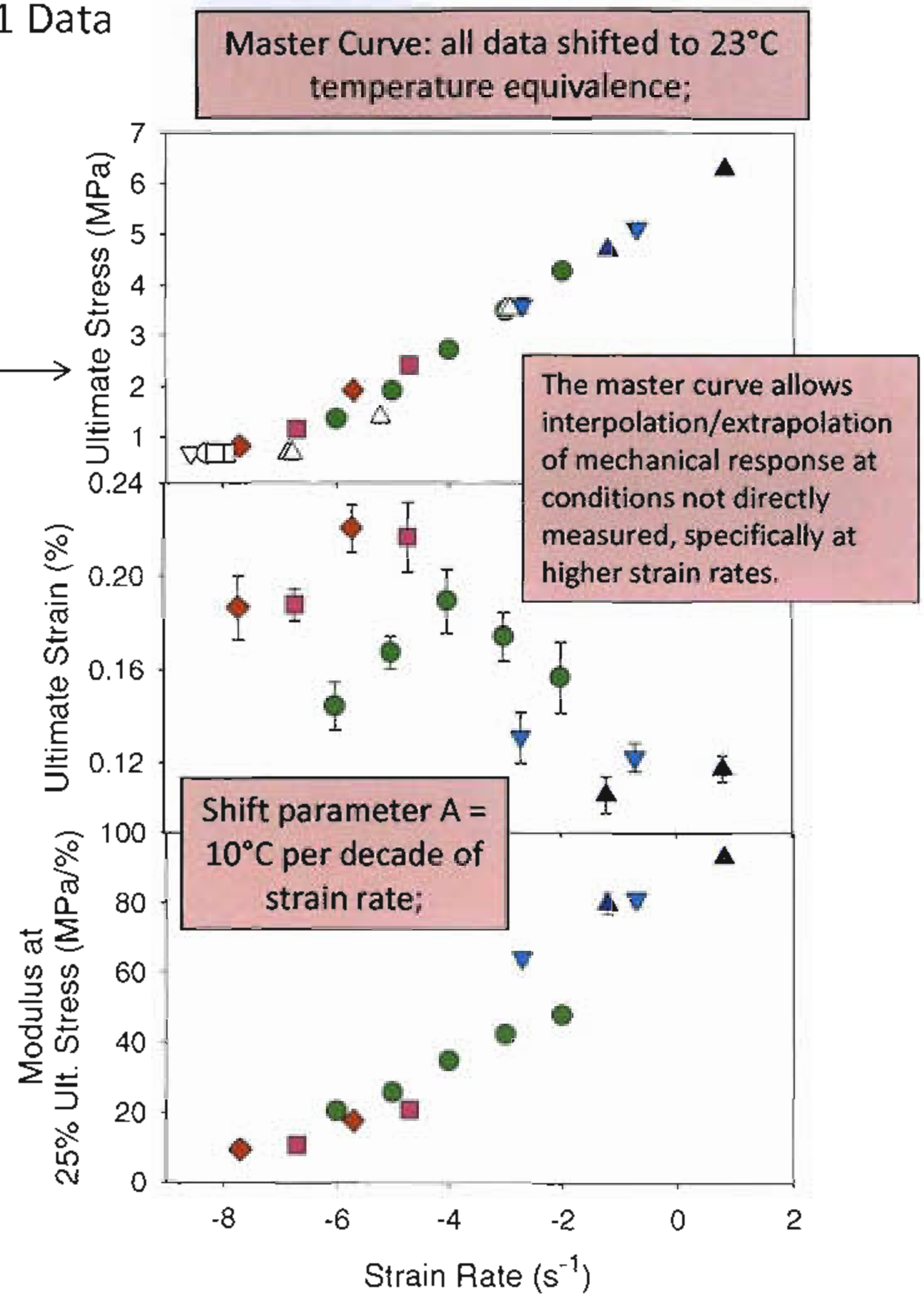
$$\log a_T = \log\left(\frac{\dot{\varepsilon}_{ref}}{\dot{\varepsilon}}\right) = \frac{1}{A}\left(T_{ref} - T\right)$$

- **Williamson, Siviour, Proud, Palmer, Govier, Ellis, Blackwell, Leppard (J. Phys. D: Appl. Phys., 2008)** ↗

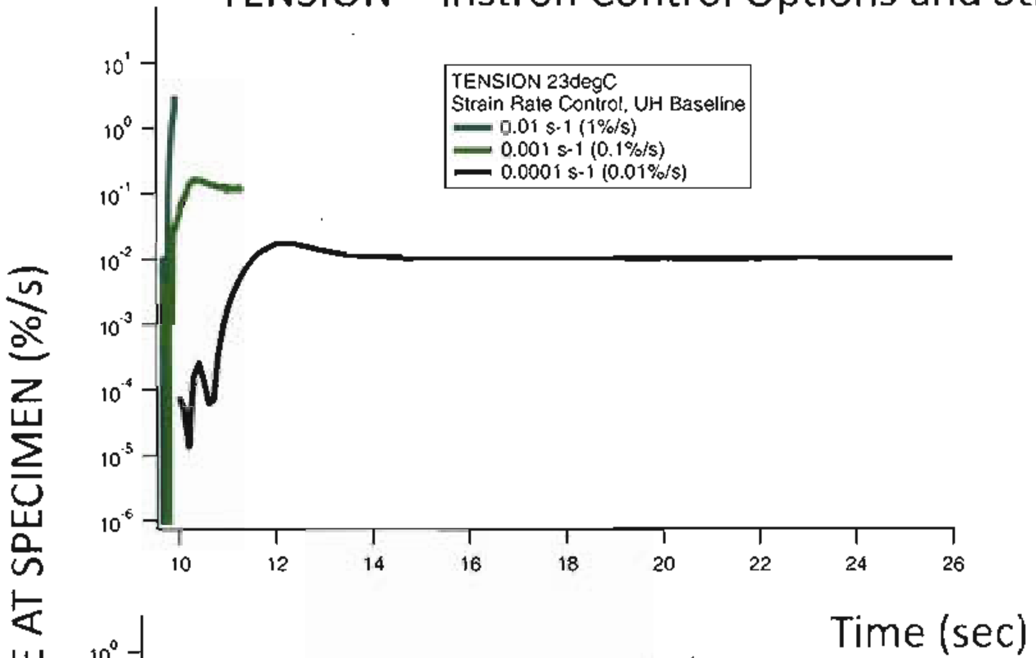
$$\text{For the HMX - based composite EDC 37, } A = \left(\frac{-13°C}{\text{rate decade}}\right)$$

Time-Temperature Analysis UH Baseline 9501 Data
Tension: Quasi-Static and Creep Results

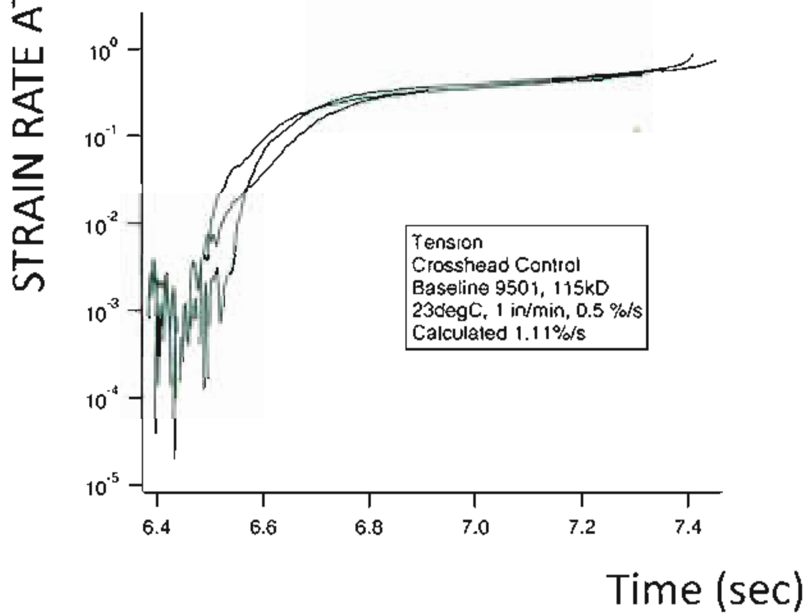




TENSION – Instron Control Options and Strain Rate at the Specimen



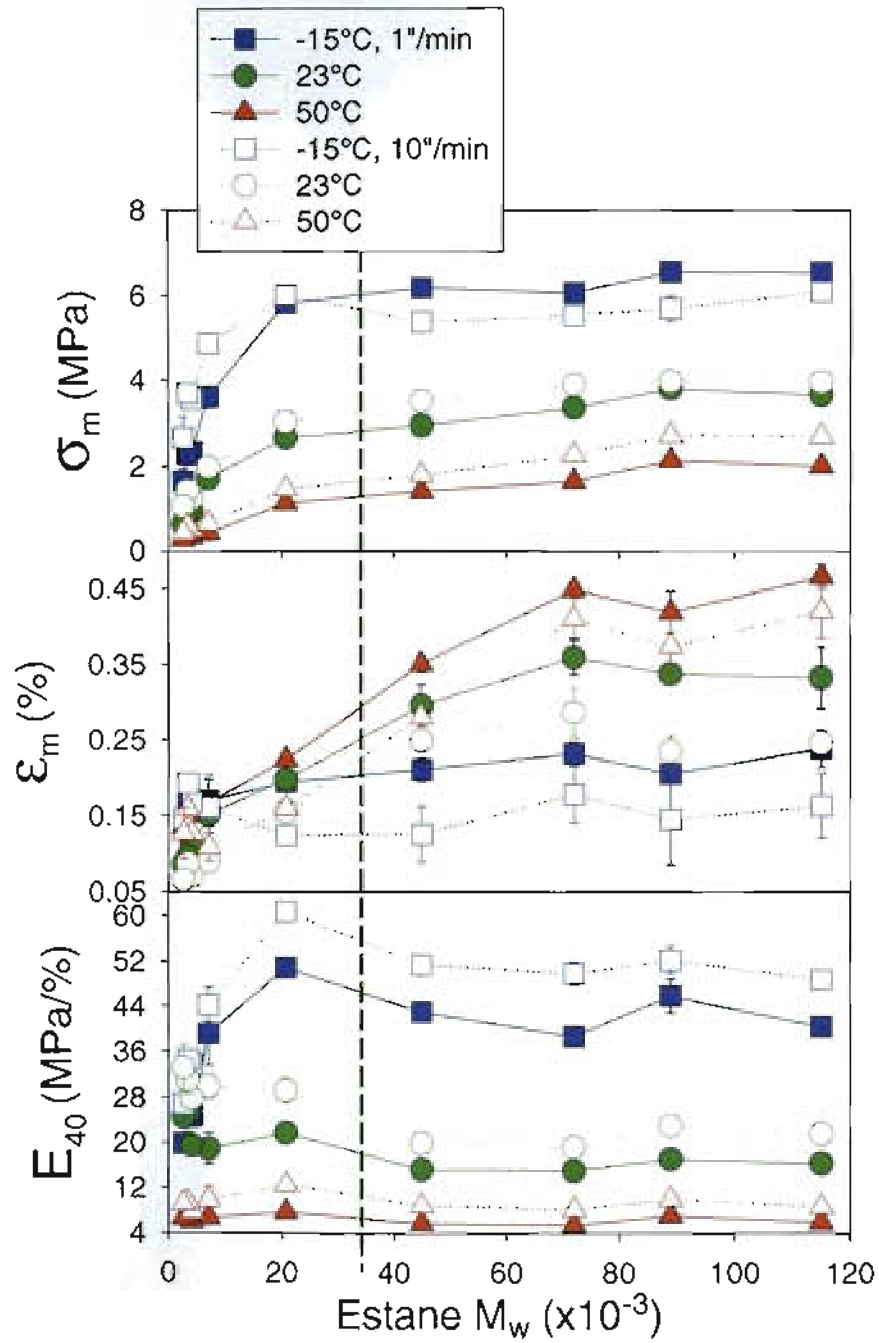
Strain Rate Controlled Tests: rate is controlled by direct feedback from averaged extensometer strain measurements; maximum strain rate is around 1%/s (0.1 s-1).



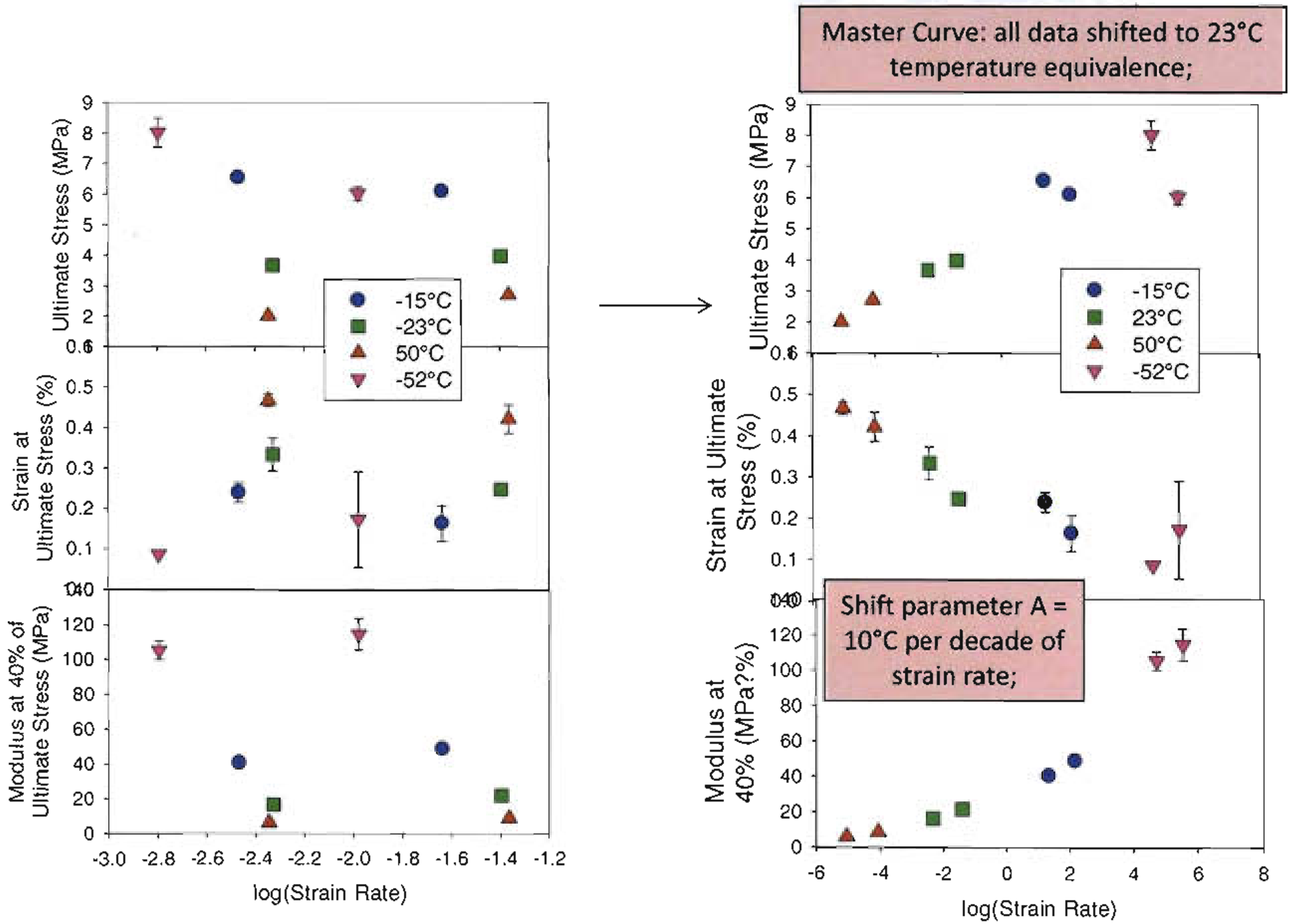
Crosshead-Controlled Tests: rate is 30 to 50% of the rate one would calculate from crosshead speed alone; must be measured/estimated using time and extensometer data; for the time-temperature analysis done here, an average strain rate was estimated for the loading part of the stress-strain curve;

Summary of Quasi-Static Tensile Results for "Virtual" and "Massively-Aged" Study

Summary of tests performed at three temperatures and two rates (see legend) as a function of Estane weight-averaged molecular weight (Mw). Each symbol is the average of 3 to 5 specimens, standard deviations shown with error bars. Data on the right of the plot, above 30kD, were from the "Virtual" study, where Estane was hydrolyzed prior to formulation. Data on the left side of the plot, below 30kD, were from the "Massively-Aged" study, where formulated PBX 9501 was hydrolyzed. The goal of these slides is to apply time-temperature analysis to all the data in these plots, forming a master curve for each Estane Mw.

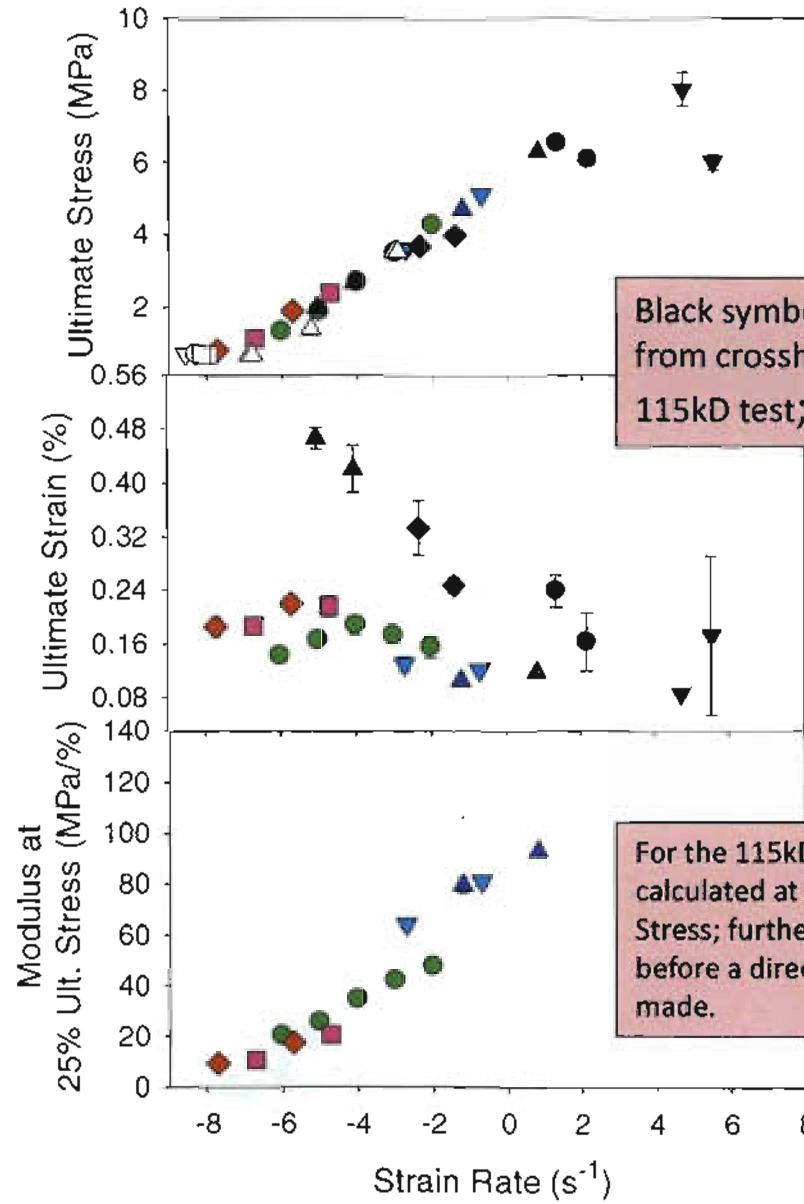


PBX 9501 TENSION from "Virtual" Aging Study, 115kD (baseline, no hydrolysis)
Crosshead Controlled Tests – Rates Measured/Estimated from Extensometers



How well do the PBX 9501 TENSION Master Curves for crosshead-controlled 115kD data overlay with the Master Curves from the strain rate-controlled UH baseline data?

Strain values from the warm (>-15°C) crosshead-controlled tests are consistently larger than strain values from the strain-rate controlled tests; not sure of the explanation for this.

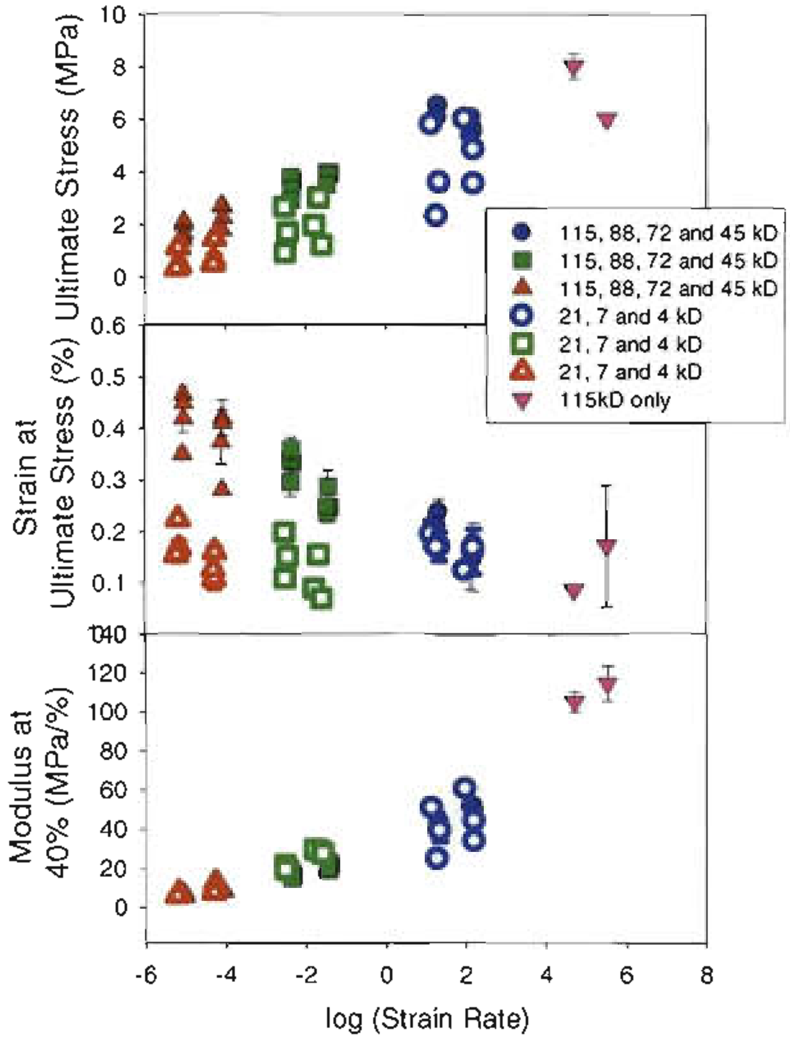


Black symbols are data from crosshead-controlled 115kD test;

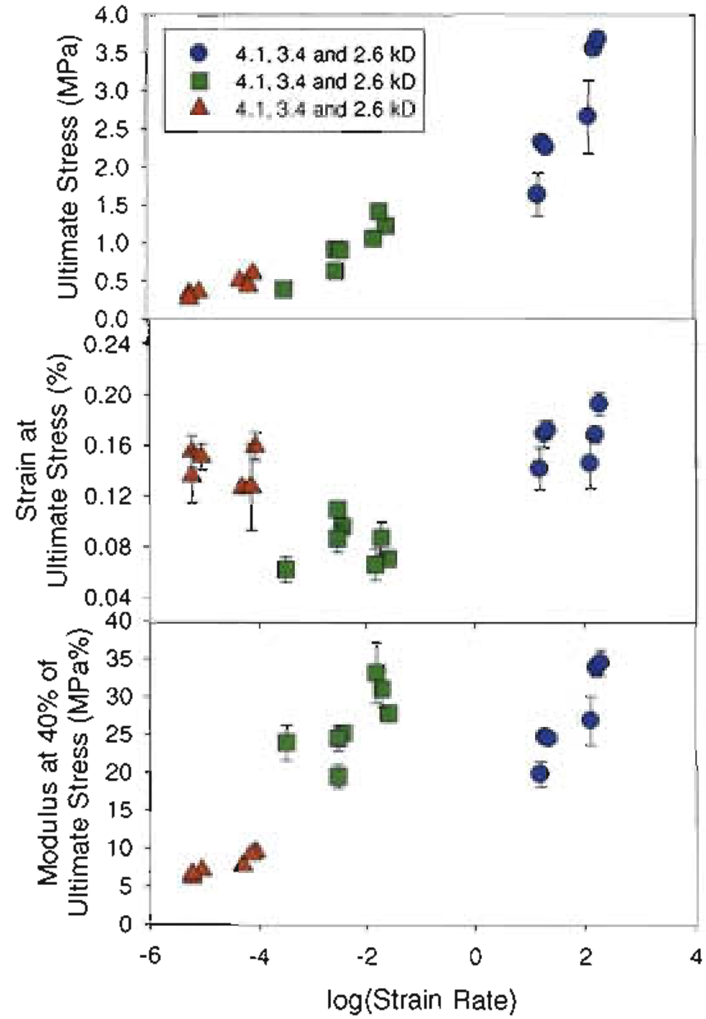
For the 115kD data, modulus was calculated at 40% of Ultimate Stress; further analysis is required before a direct comparison can be made.

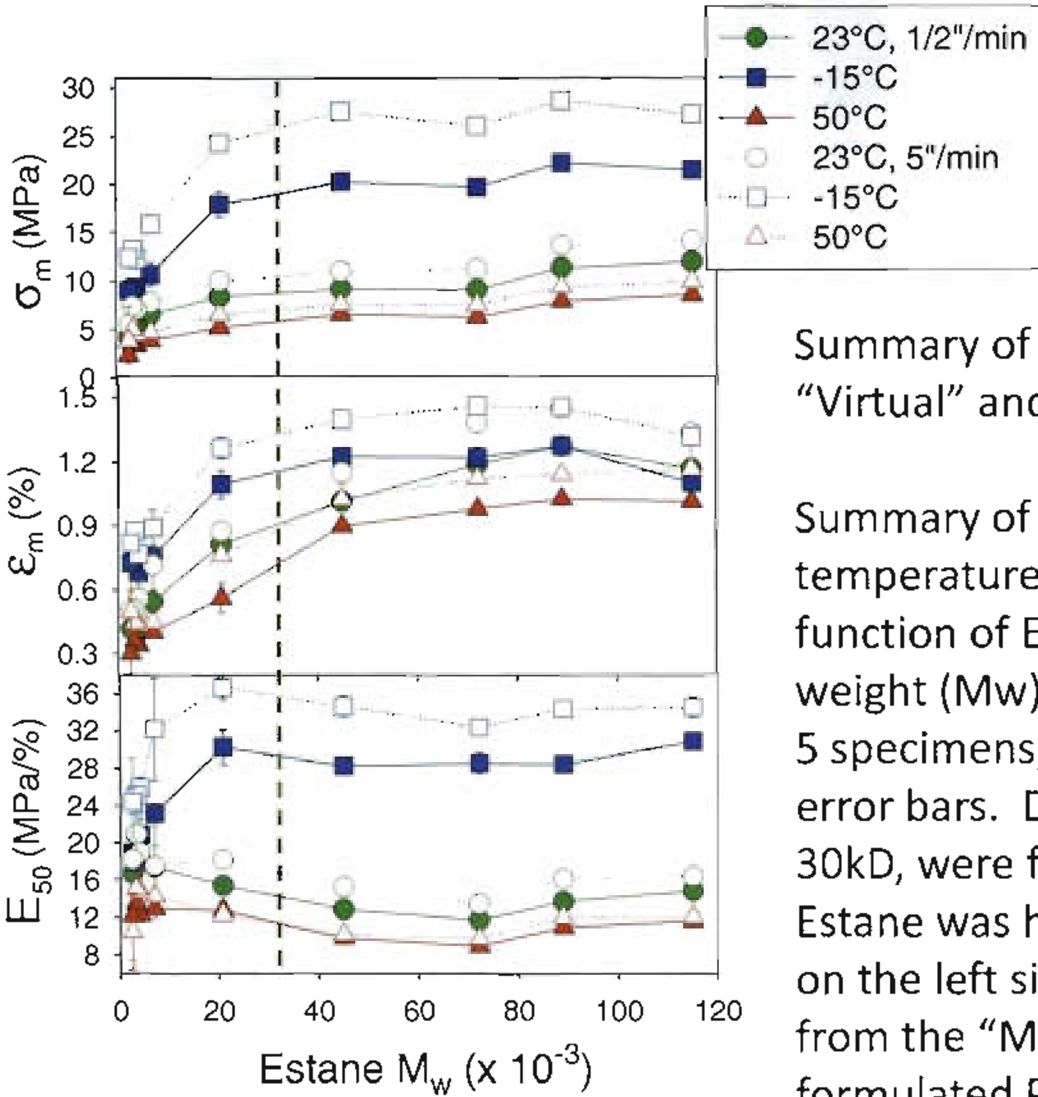
All tensile Master Curve data shifted to 23°C temperature equivalence using 10°C per decade of strain rate; ;

Degradation of Master Curves with Decreasing Estane Mw (see legend)



Master Curve of PBX 9501 with Reduced Estane Mw (2 to 4 kD)

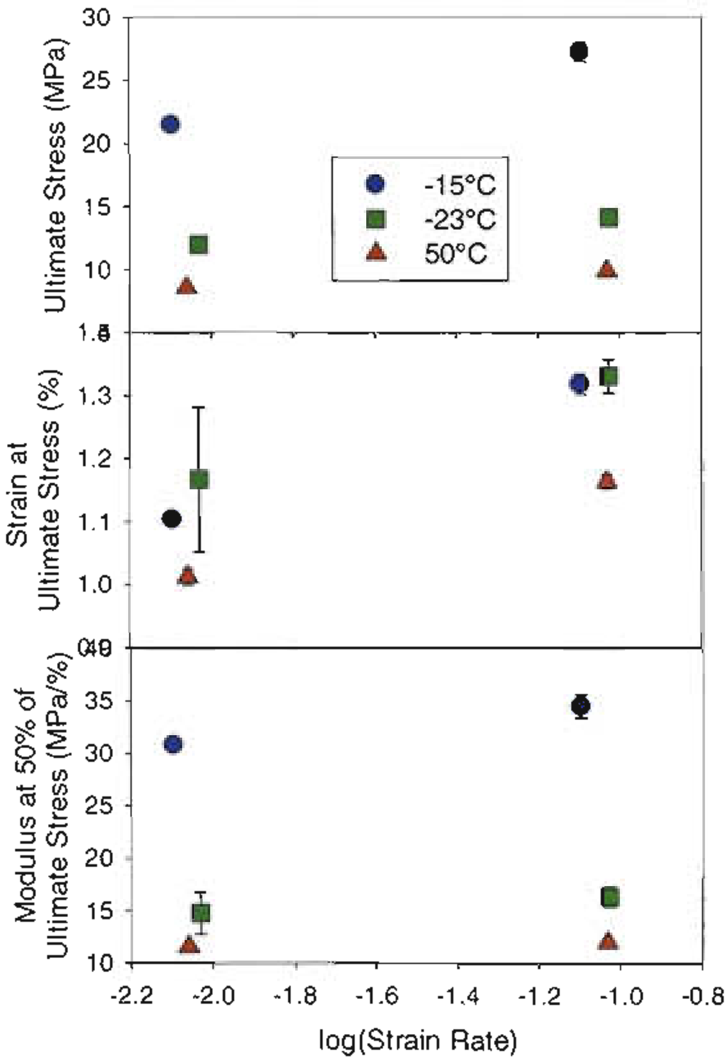


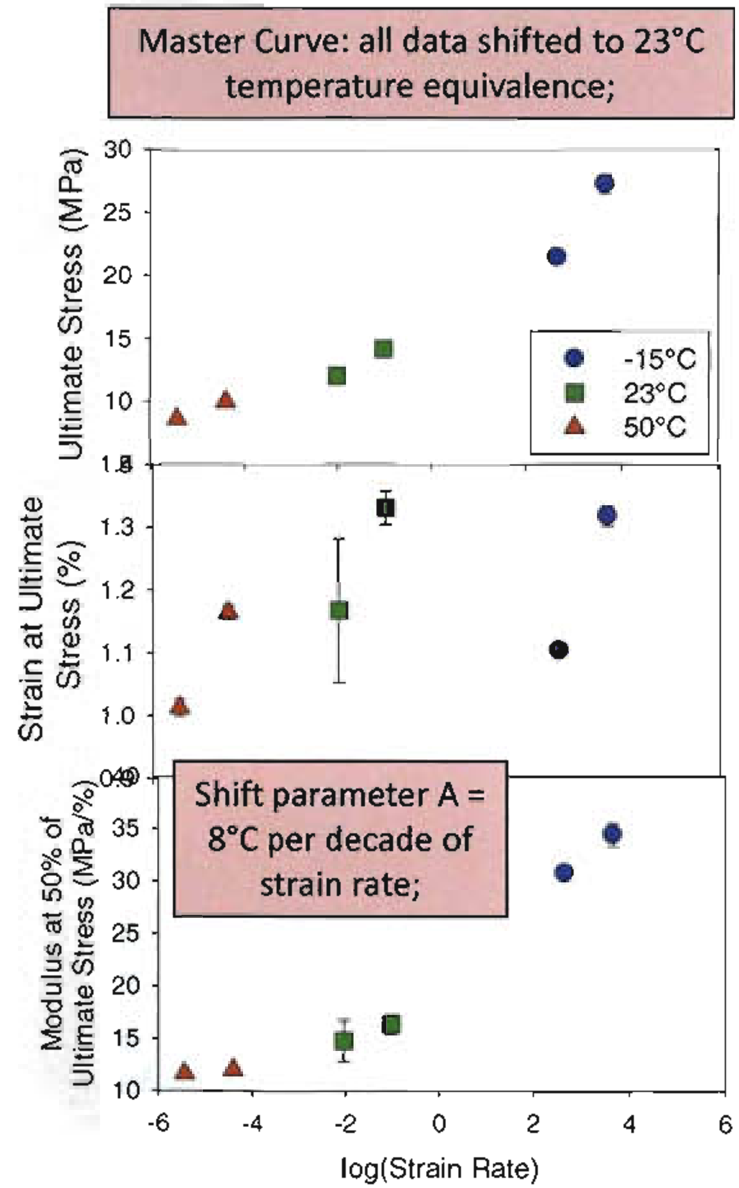


Summary of Quasi-Static Compression Results for "Virtual" and "Massively-Aged" Study

Summary of tests performed at three temperatures and two rates (see legend) as a function of Estane weight-averaged molecular weight (Mw). Each symbol is the average of 3 to 5 specimens, standard deviations shown with error bars. Data on the right of the plot, above 30kD, were from the "Virtual" study, where Estane was hydrolyzed prior to formulation. Data on the left side of the plot, below 30kD, were from the "Massively-Aged" study, where formulated PBX 9501 was hydrolyzed. The goal of these slides is to apply time-temperature analysis to all the data in these plots, forming a master curve for each Estane Mw.

Baseline PBX 9501 COMPRESSION from Aging Studies, 115kD
Crosshead Controlled Tests – Rates Measured/Estimated from Extensometers



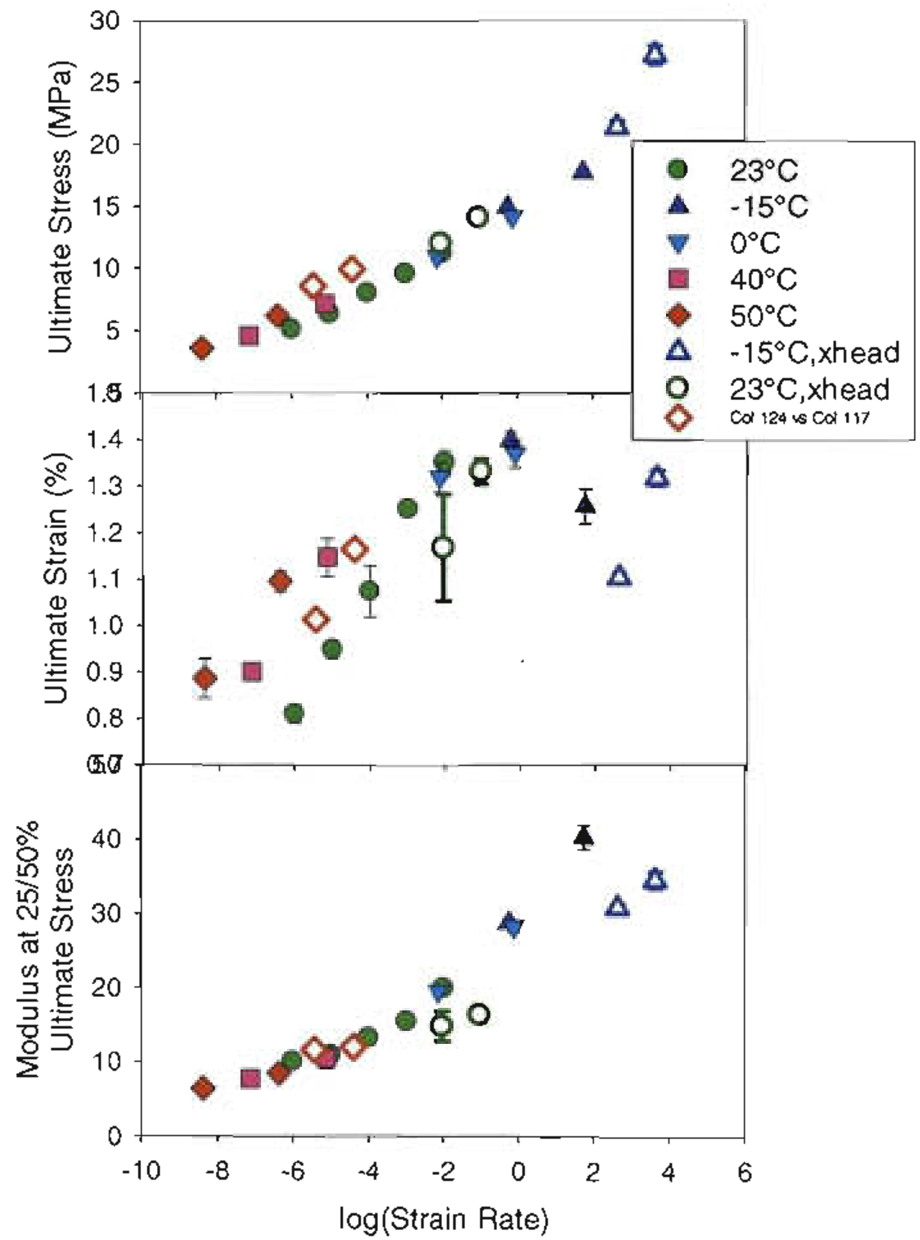


How well do the COMPRESSION Master Curves for crosshead-controlled data ("Virtual" aging study, 115kD baseline) overlay with the Master Curves from the strain rate-controlled UH baseline data?

Closed symbols: strain rate controlled UH baseline

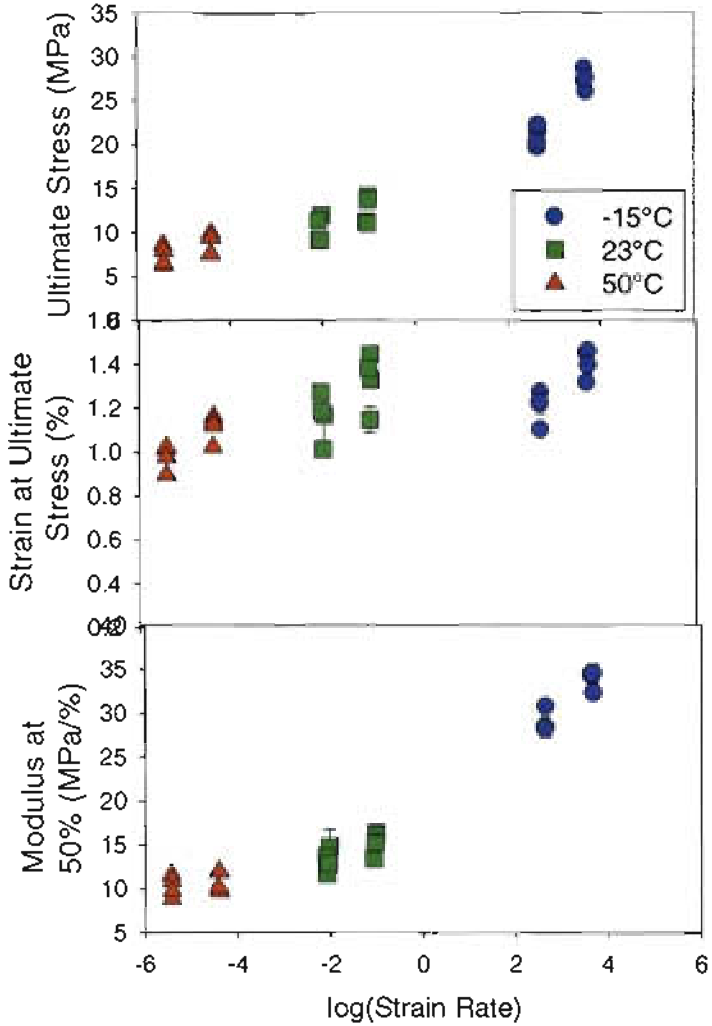
Open symbols: crosshead controlled "virtual" aging baseline, 115kD;

Modulus calculated at 25% of ultimate stress for strain rate controlled data, 50% of ultimate stress for crosshead-controlled data, so comparison is not direct.

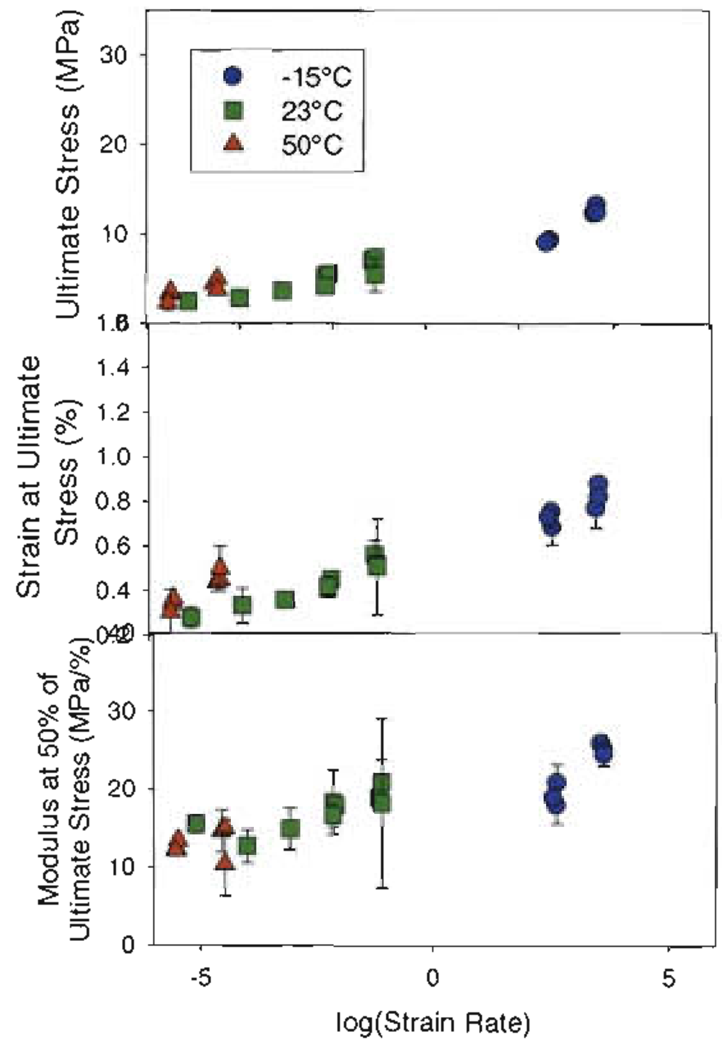


All compressive Master Curve data shifted to 23°C temperature equivalence using 8°C per decade of strain rate;

Degradation of Master Curves with Decreasing Estane Mw (115, 88, 72 and 45 kD)



Master Curve of PBX 9501 with Reduced Estane Mw (2 to 4 kD)



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