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# Stress–strain behavior of a polyurea and a polyurethane from low to high strain rates

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## Abstract

The large deformation stress–strain behavior of thermoplastic–elastomeric polyurethanes and elastomeric-thermoset polyureas is strongly dependent on strain rate. Their mechanical behavior at very high strain rates is of particular interest due to their role as a protective coating on structures to enhance structural survivability during high rate loading events. Here we report on the uniaxial compression stress–strain behavior of a representative polyurea and a representative polyurethane over a wide range in strain rates, from 0.001 $s^{-1}$ to 10,000 $s^{-1}$, successively marching through each order of magnitude in strain rate using equipment relevant for testing at each particular rate. These results are further analyzed in association with recently reported compressive data on the same materials by Yi et al. [Polymer 2006;47(1):319–29] and intermediate rate tensile data on the same polyurea by Roland et al. [Polymer 2007;48(2):574–8]. The polyurea tested is seen to undergo transition from a rubbery-regime behavior at low rates to a leathery-regime behavior at the highest rates, consistent with the earlier compression study as well as the recent tension study; the polyurethane tested is observed to undergo transition from a rubbery-regime behavior at the low rates to a glassy behavior at the highest rates. The uniaxial compression data for the polyurea are found to be fully consistent with the recently reported uniaxial tension data over the range of rates studied, demonstrating the consistency and complementary aspects of testing at high rates in both compression and tension.

*Keywords:* Polyurea; Polyurethane; Stress–strain behavior

## 1. Introduction

Elastomeric-like polyurea and polyurethanes offer a wide range in mechanical behavior due to the ability to tailor the underlying hard and soft domain structure through chemistry. Due to the versatility of these materials and their commercial viability in a myriad of applications, their large deformation behavior over a wide range in strain rates is of interest, particularly for those formulations where the polymer glass transition regime is near the temperature of use. Previous studies on a polyurea and three polyurethanes by Yi et al. [1] provided a first set of data quantifying the stress–strain behavior of these materials at low strain rates ($<1\ s^{-1}$) in comparison to their behavior at very high rates ($>10^3\ s^{-1}$), showing different transitions in mechanical behavior depending upon the particular chemistry and the location of the glass transition temperature. The polyurea displayed a transition from rubbery behavior at low rates to leathery behavior at the very high rates, whereas, one of the three polyurethanes displayed a transition from rubbery behavior at low rates to glassy-like behavior at the high rates. These transitions were observed to be consistent with the shift in mechanical glass transition ($T_g$) with strain rate, measured using dynamic mechanical analysis (DMA), as shown in the DMA data shown in Figs. 2–4 of [1]. However, the transition in the stress–strain behavior as strain rate increases has not been fully characterized due to experimental limitations in accessing the full range in

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strain rates. More recently, Roland et al. [2] have characterized the same polyurea under uniaxial tension at intermediate strain rates (~10 $s^{-1}$–300 $s^{-1}$) using a newly developed drop weight tensile testing instrument. In the present paper, the understanding of the rate dependent behavior of these materials is further studied in uniaxial compression by accessing strain rates which march through each order of magnitude in the strain rate range of $10^{-3}$ $s^{-1}$–$10^{4}$ $s^{-1}$. These results are analyzed in association with previously reported data [1,2] to elucidate the dependence of the stress–strain behavior on strain rate and compare/contrast the mechanical behaviors observed in uniaxial compression with those observed in uniaxial tension where available.

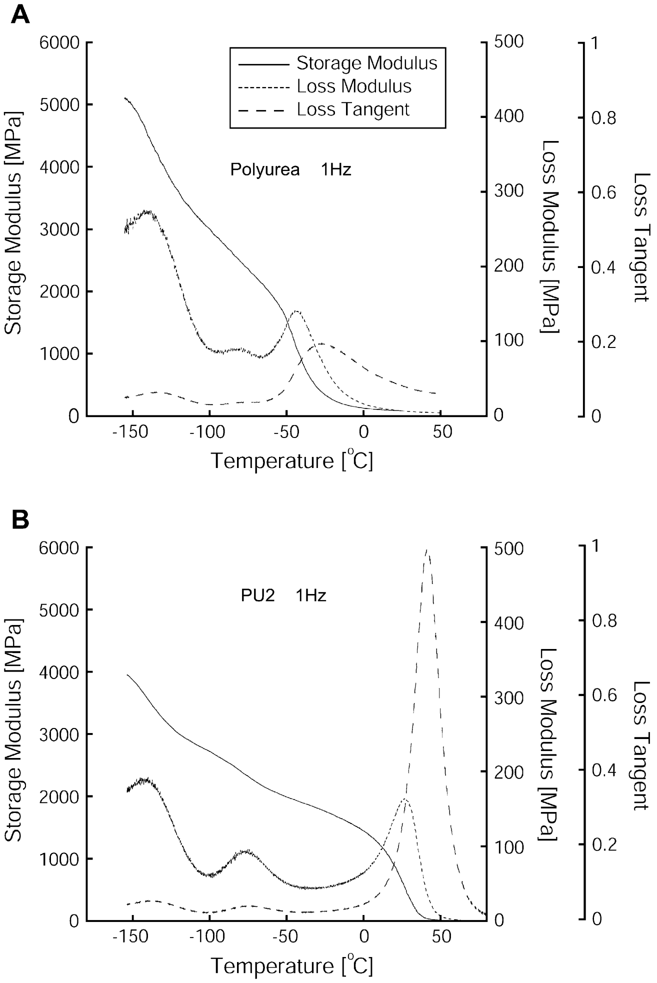

Fig. 1. Dynamic mechanical analysis data for the polyurea and the PU2 at a frequency of 1 Hz (reproduced from [1]). The loss tangent was found to shift by 4.0 K (polyurea) and 4.7 K (PU2) per factor of 10 increase in frequency.

## 2. Experimental protocol

### 2.1. Materials

The chemical compositions and the segment ratios for the polyurea and the polyurethane materials of this study are enumerated in [1], wherein they are referred to as polyurea and PU2, respectively. The polyurea of the Roland et al. study is described in [2] and is the same or nearly the same polyurea as that studied by Yi et al. [1]. For later comparison purposes, the DMA data for the polyurea and the PU2 from [1] are repeated here in Fig. 1; using the peak in the tan($\delta$) as a measure of "$T_g$", the $T_g$ was found to shift 4.0 K and 4.7 K per factor of 10 increase in test frequency.

Cylindrical specimens for mechanical testing were punched from the supplied sheets. Due to the compliant behavior of the materials and their deformation during the punching, the resulting specimens have a slight axial taper. The specimen surfaces which contact the test machine were lubricated with thin PTFE sheets and/or petroleum jelly (applied immediately prior to testing) to minimize any surface friction and ensure uniform homogeneous deformation conditions.

### 2.2. Test procedures

#### 2.2.1. Low to intermediate rate

The low to moderate rate compression tests (nominal strain rates of $10^{-3}$ $s^{-1}$–$10^{-1}$ $s^{-1}$) were performed using a Zwick screw driven mechanical tester at the Massachusetts Institute of Technology (MIT) under conditions of constant nominal strain rate. Moderate to intermediate rate tests (1 $s^{-1}$–$10^{2}$ $s^{-1}$) were conducted on an enhanced servo hydraulic MTS 810 machine at Purdue University under various imposed engineering strain rate conditions.

#### 2.2.2. Intermediate to high rate

The materials were also tested in uniaxial compression at strain rates in the $10^{2}$ $s^{-1}$–$10^{3}$ $s^{-1}$ range using an intermediate rate split Hopkinson pressure bar (SHPB) at Purdue University. The 19 mm diameter bars (incident bar length = transmitted bar length = 11 m, striker bar length = 3 m) were constructed from aluminum to reduce the stiffness mismatch with the polymeric samples in order to increase the transmission signal for purposes of measuring the stress transmitted to the polymer. Annealed copper discs were used as pulse shapers to help improve dynamic equilibrium and also dampen the high frequency components in the stress pulses thus reducing dispersive effects. The complete operational and design details of split Hopkinson bar techniques for testing of polymeric materials can be found in [3] and [4]. The high rate tests (>1000 $s^{-1}$) were performed on an SHPB (19 mm diameter, aluminum 7075 T6 bars; incident bar length = transmission bar length = 2.9 m; striker bar length = 51 cm) at the MIT Institute for Soldier Nanotechnologies; see [5] for further description of this SHPB set-up. Some tests were coupled with a Cordin 550 rotating mirror CCD camera to obtain high-speed images of specimens during the dynamic deformation. Fig. 2 shows representative high-speed photographs captured at the indicated strain levels during a high rate test on polyurea at a strain rate of ~7500 $s^{-1}$. The sample is seen to deform uniformly, obtaining nearly homogeneous uniaxial compression deformation over the entire strain history. Note that the small initial taper of the specimen is retained during compression and does not influence the homogeneity of the deformation or the uniaxial stress aspect of the test in any significant manner. Additionally, dynamic

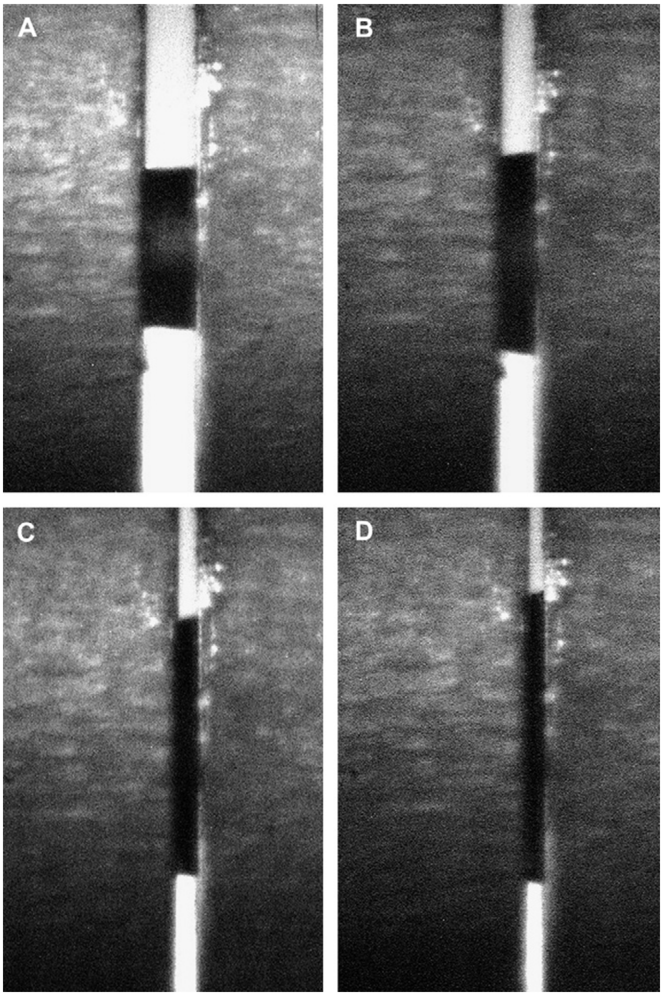

Fig. 2. Photographs recorded during a high strain rate compression test on polyurea at a strain rate of 9000 $s^{-1}$, showing the homogeneity of the deformation. Note that specimens are punched from a sheet, resulting in a slight initial taper to the specimen which is retained with deformation. (A) $\varepsilon \sim 0$, (B) $\varepsilon \sim 0.4$, (C) $\varepsilon \sim 0.75$, and (D) $\varepsilon \sim 1$.

equilibrium was monitored by comparing the time-resolved force history at the front (incident) and back (transmission) faces of the specimen, see Fig. 3. At very high strain rates, dynamic equilibrium was generally observed to be reached by strain levels $\leq 0.3$ for the very compliant cases (i.e., for the rubbery and leathery regimes); equilibrium was reached by even smaller strain levels for tests at the lower end of SHPB strain rate range. As one transitioned to a more glassy-like response, dynamic equilibrium was achieved at a strain of $\sim$0.07 just prior to yield. Following common practice, the portion of the stress–strain curves prior to reaching dynamic equilibrium is not considered accurate.

## 3. Results and discussion

### 3.1. Polyurea

The uniaxial compressive stress–strain behavior of polyurea was examined using the techniques described in Section 2.2.

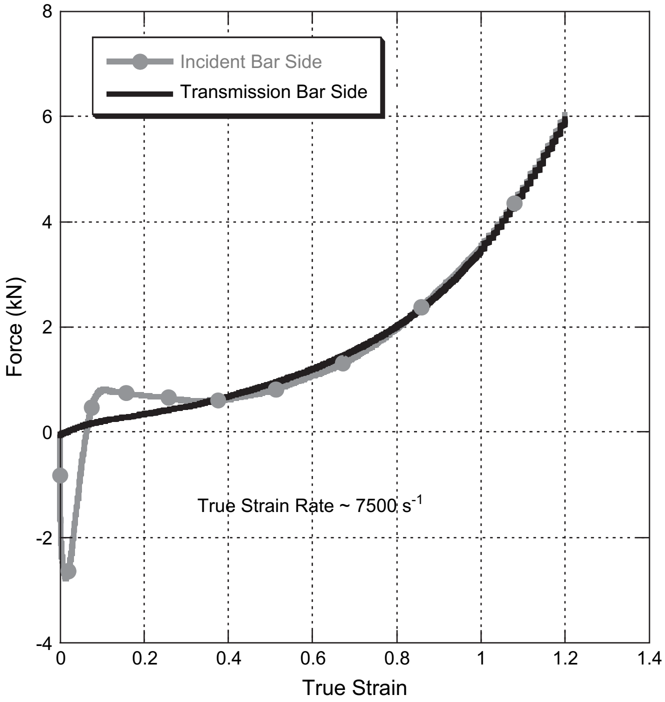

Fig. 3. A comparison of forces recorded at the incident bar side and the transmission bar side of the specimen for a sample test at $\sim$7500 $s^{-1}$ to monitor the dynamic equilibrium.

The true stress–true strain curves for polyurea over seven decades of strain rate are presented in Fig. 4A. For the SHPB cases, the corresponding histories of true strain rate as a function of true strain are shown in Fig. 4B. As shown in Fig. 4B, for the intermediate strain rate tests, the *true* strain rate shows a modest increase with increase in true strain whereas, for the highest rate tests, the *true* strain rate monotonically increases by a factor of 1.5–2 from a true strain of 0.0 to a true strain of 1.2. The inset of Fig. 4B shows a comparison of the *engineering strain rate versus engineering strain* to that of the corresponding *true strain rate versus true strain* for three high rate SHPB tests, and an SHPB test with pulse shaper, showing the *engineering* strain rate to be relatively constant over the course of a test for all the cases. Noting how the strain rate varies over the course of each SHPB test, each true stress–true strain curve is identified by its *true* strain rate taken at a true strain of 0.60.

The uniaxial compressive stress–strain behavior is observed to be rate dependent and highly non-linear. The curves show an initially relatively stiff behavior followed by a rollover to a more compliant behavior at low strains, with the stress magnitude depending on strain rate. The stress levels are seen to span from a few MPa to nearly 100 MPa depending on the magnitude of strain and strain rate. As expected, the low and high rate data are fully consistent and overlap with those obtained and reported earlier in [1]. The data over the strain rate range from 1 $s^{-1}$ to 2000 $s^{-1}$ are found to follow the basic expected trend in the dependence of the stress–strain behavior on strain rate, filling in the wide gap in strain rate that had remained vacant in the Yi et al. study. The polyurea

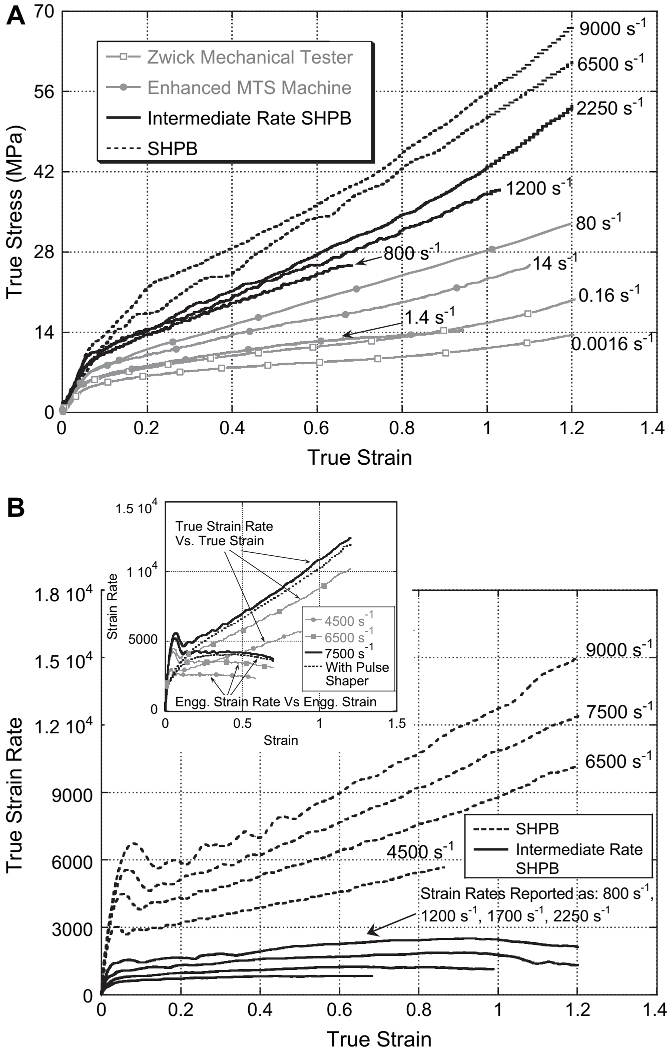

Fig. 4. (A) Uniaxial compression stress–strain behavior of polyurea at strain rates ranging from $10^{-3}\ \mathrm{s}^{-1}$ to $9000\ \mathrm{s}^{-1}$ (each SHPB curve is labeled by its true strain rate at a true strain of 0.60; complete strain rate histories as a function of true strain for the SHPB cases are in (B)). (B) Entire *true strain rate* ($\mathrm{s}^{-1}$) *versus true strain* profiles for the SHPB and the intermediate rate SHPB; inset shows the comparison of *true strain rate* ($\mathrm{s}^{-1}$) and *engineering strain rate* ($\mathrm{s}^{-1}$) profiles for three sample high rate SHPB tests and a sample SHPB test with an annealed copper pulse shaper.

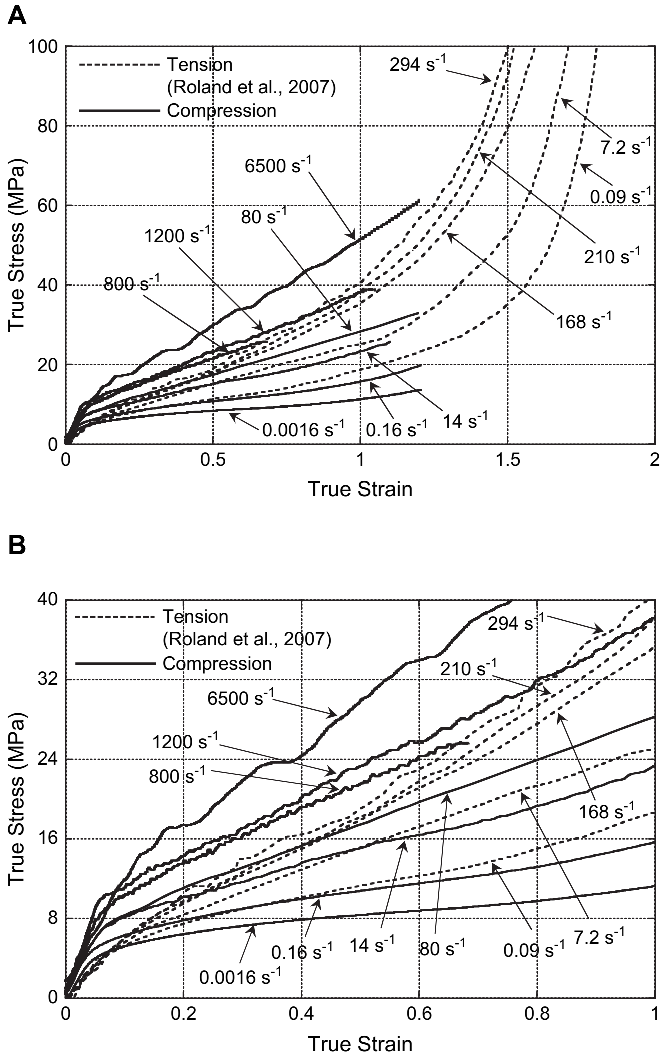

Fig. 5. (A) A comparison of the compression test data of polyurea with recently reported tensile data [2] at comparable strain rates (the true strain rates for the tensile tests are those estimated at ∼0.7 true strain for the tensile [2] data utilizing the reported engineering strain rates and a sample engineering strain rate evolution profile). (B) 'Zoom in' of A up to a true strain of 1.0.

stress–strain curves are observed to transition from a compliant rubber-like behavior at the lowest strain rates to a leathery-regime behavior at the high strain rates (as indicated by the increased flow stress magnitudes) consistent with the DMA data of Fig. 1 and its shift with rate as reported in [1].

Recently, Roland et al. [2] have reported uniaxial tension data for this polyurea at true strain rates ranging from $\sim 0.1\ \mathrm{s}^{-1}$ to $300\ \mathrm{s}^{-1}$ using a newly developed drop weight test instrument. Using this instrument, the samples were elongated until failure; the sample force was calculated after compensating for the inertial effects of the instrument and the strain in the sample was measured by monitoring fiducial marks through high-speed photography. Fig. 5 shows a plot of the Roland et al. tensile data together with the compression data (in terms of the magnitude of true stress versus the magnitude of true strain) of this study (noting that our low and high rate data are coincident with those in the Yi et al. study). Fig. 5A shows the data sets out to the largest strains tested for each case; Fig. 5B shows a "zoom-in" of these data to a maximum true strain of 1.0. As seen in Fig. 5B, the tensile test data [2] are in good agreement with the compressive test data at similar strain rates. Note that Roland et al. [2] report their strain rate in terms of the average *engineering* strain rate over the course of a test. Due to the large deformations incurred in these tests, it is also appropriate to examine the *true* strain rate history over the course of a test. Roland et al. report one typical engineering strain rate ($\dot{e}$) history as a function of engineering strain, reproduced here in Fig. 6. These data are easily converted to true strain rate ($\dot{\varepsilon} = \dot{e}/(1+e)$) as a function of true strain ($\varepsilon = \ln(1+e)$) and are shown in the plot of Fig. 5, giving the true strain rate versus true strain history that corresponds to the tensile true stress–true strain data of the "average engineering strain

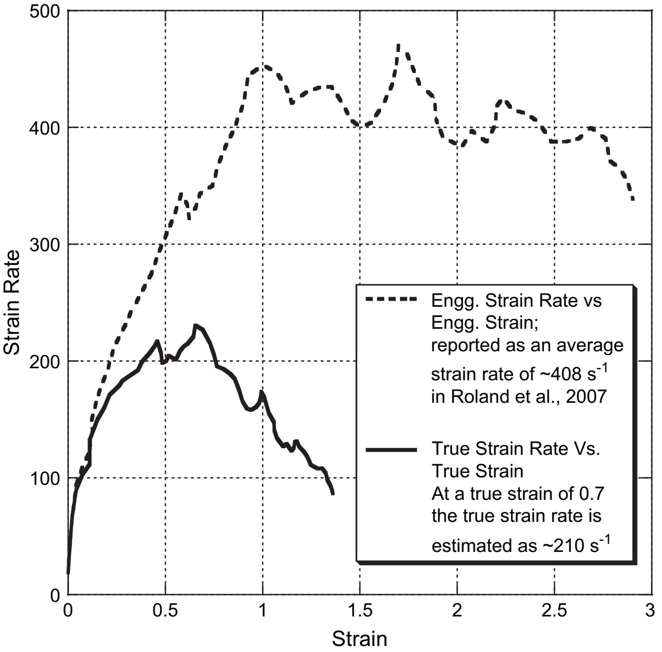

Fig. 6. A sample *engineering* strain rate (s$^{-1}$) versus *engineering* strain plot reported in [2], and its corresponding *true* strain rate (s$^{-1}$) versus *true* strain profile.

rate of 408 s$^{-1}$" of Figs. 5 and 6 of [2]. The engineering strain rate is found to increase by a factor of 4 up to an engineering strain of 1.0 and then to be relatively constant; the true strain rate is found to increase by a factor of 2 up to a true strain of 0.70 and then monotonically decrease by a factor of about 2 between a true strain of 0.70 and 1.40.

As seen in a comparison of the tension and compression data to large strain (Fig. 5A), the nature of the stress–strain curves in compression and tension and the stress levels attained for a given strain rate and strain level are similar for strains less than 1.0. Given the compression versus tension aspects of the two sets of data, one might anticipate differences at small to moderate strains due to a pressure effect. However, due to the compliant aspect of this material at this temperature, the stress levels during uniaxial loading are low (tens of MPa) with correspondingly low pressures, and therefore it is difficult to discern any pressure effect especially given that the strain rate is such a large effect on these data and the strain rate histories for the different data sets differ with strain.

At the larger magnitudes of the strains tested, the classic contrast in stiffening observed between uniaxial tension and uniaxial compression of rubbery and/or glassy polymers is observed in Fig. 5. During uniaxial tensile stress loading conditions, the molecular orientation evolves towards a uniaxial orientation which results in dramatic stiffening (up turn in the stress–strain curve) beginning at a smaller strain (~1.1) in tension than that observed during uniaxial compression. During uniaxial compressive stress loading conditions, molecular orientation evolves in a biaxial manner with chains orienting biaxially in the plane normal to the compression axis (see, for example [6–8]) and, for this material, dramatic stiffening has not yet taken place even at the largest compressive strains tested.

Since the polyurea did not display a distinct yield behavior, the value of stress taken at prescribed strain magnitudes is plotted as a function of the true strain rate to more thoroughly gage the rate sensitivity. Fig. 7 plots the stress levels at true strains of 0.4 and 0.9 as a function of the true strain rate on a logarithmic scale using the compression data from the curves in Fig. 4 and the tension data from Fig. 5. (For the Roland et al. data, we have assumed their engineering strain rate history for each case follows the trend of their reported typical engineering strain rate in order to determine a reasonably accurate value for their true strain rate at each true strain). At strain rates higher than 10 s$^{-1}$, the material shows a significant increase in rate sensitivity as evidenced by the greater rise in stress levels with increasing strain rate. The stress levels for the tensile test curves [2] are also plotted in Fig. 7 for comparison. No discernable difference is observed between the tensile and the compressive stress data at a strain of 0.40, implying no appreciable pressure dependence over this small range in pressure (where the maximum range in pressure between tension and compression at a strain of 0.40 goes from −5 MPa to +5 MPa; given that a typical $T_g$ shift with pressure is approximately 0.2 K/MPa [9], it would be surprising to see any significant effect of pressure on this behavior). At large strains (true strain = 0.9), the flow stress levels in tension are seen to be slightly higher in comparison to those in compression. As indicated earlier, the difference in the tension and compression stress–strain curves at large strains can be attributed to a greater molecular orientation induced stiffening in tension than in compression: under tension the molecular chains undergo an axial alignment along the direction of elongation, whereas in compression, the chains undergo a biaxial alignment in the plane normal to the compression axis.

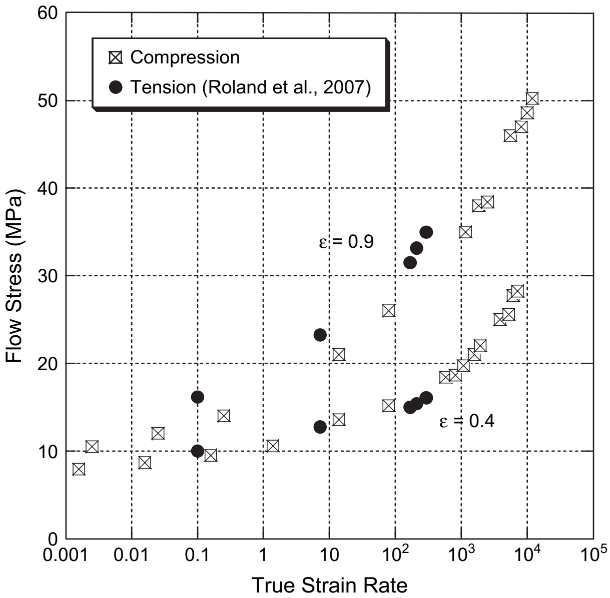

Fig. 7. Stress (taken at true strain values of 0.4 and 0.9) as a function of true strain rate (from low to high strain rates (s$^{-1}$), where the value for true strain rate used for each point is also taken at its respective true strain value of 0.4 or 0.9) plotted for polyurea. Boxes are from the compression data of Fig. 4; solid circles are tension data from [2] data of Fig. 5.

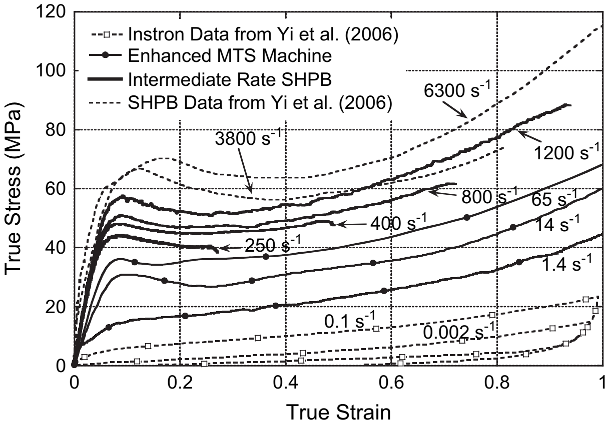

Fig. 8. Stress–strain behavior of polyurethane under compression at strain rates ranging from 0.002 s$^{-1}$ to 6300 s$^{-1}$. The data for the low and high rate tests (shown as dotted lines) are reproduced from [1].

### 3.2. Polyurethane

Similarly, uniaxial compression tests were performed on the polyurethane at previously un-accessed strain rates in the 1 s$^{-1}$–10$^{3}$ s$^{-1}$ range using the enhanced MTS and intermediate rate SHPB. The true stress–strain curves for these tests are overlaid with low rate and high rate data for the same material taken from [1] in Fig. 8. At low rates the behavior is again observed to be rate sensitive and non-linear showing a rollover to flow at low strains. As the strain rate is increased, the material transitions from a rubbery behavior at the lowest rates ($\sim 10^{-3}$ s$^{-1}$) to a leathery response ($\sim 1$ s$^{-1}$) to a glassy behavior ($\sim 1000$ s$^{-1}$). The curves at strain rates greater than or equal to 14 s$^{-1}$ show a distinct yield point. To assess the rate sensitivity of polyurethane, the yield stress is plotted against strain rate in Fig. 9. For the low rate curves, wherein the curves did not display a distinct yield point, the stress at the corresponding strain was used. The figure shows a marked increase in rate sensitivity at strain rates greater than 1 s$^{-1}$, as the material transitions through the rubbery to the leathery to the glassy regimes, consistent with the DMA data of Fig. 1 and its reported shift with rate detailed in [1].

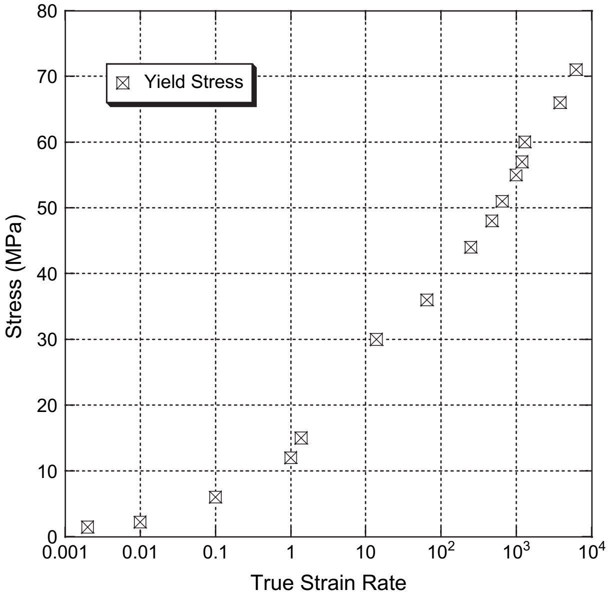

Fig. 9. Yield stress as a function of true strain rate for polyurethane.

## 4. Summary

In this study the transitions in mechanical behavior for a polyurea and a polyurethane have been examined over seven orders of magnitude of strain rate using novel experimental techniques. Access to such strain rates helped to precisely characterize the strong dependence of the stress–strain behavior on strain rate and how the behavior gradually undergoes transitions from rubbery to leathery to glassy behavior with increasing strain rate (where the polyurea transitions from rubbery at the low rates ($\sim 0.001$ s$^{-1}$) to leathery at high rates ($\sim 5000$ s$^{-1}$) and the PU2 polyurethane transitions from rubbery ($\sim 0.002$ s$^{-1}$) to leathery ($\sim 0.1$ s$^{-1}$) to glassy ($\sim 1000$ s$^{-1}$)). The compressive test results of polyurea are also seen to be in good agreement with recently reported data in tension [2] at similar strain rates. These transitions were observed to be consistent with the shift in mechanical glass transition ($T_g$) with strain rate, measured using dynamic mechanical analysis.

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## References

[1] Yi J, Boyce MC, Lee GF, Balizer E. Polymer 2006;47(1):319–29.
[2] Roland CM, Twigg JN, Vu Y, Mott PH. Polymer 2007;48(2):574–8.
[3] Gray III GT, Blumenthal WR. ASM handbook, mechanical testing and evaluation. 10th ed., vol. 8. Materials Park, OH: ASM International; 2000. p. 488–96.
[4] Chen W, Lu F, Frew DJ, Forrestal MJ. Journal of Applied Mechanics – Transactions of the ASME 2002;69:214–23.
[5] Mulliken AD. PhD thesis, Department of Mechanical Engineering, Massachusetts Institute of Technology; 2006.
[6] Treloar LRG. The physics of rubber elasticity. Oxford: Clarendon Press; 1975.
[7] Arruda EM, Boyce MC. International Journal of Plasticity 1993;9:697–720.
[8] Arruda EM, Boyce MC. Journal of the Mechanics and Physics of Solids 1993;41:389–412.
[9] Ferry JD. Viscoelastic properties of polymers. 3rd ed. New York: John Wiley & Sons; 1980 [chapter 11].