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12-01157

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Intended for: Proceedings of SEM 2012

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Large-Strain Time-Temperature Equivalence and Adiabatic Heating of Polyethylene

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ABSTRACT

Time-temperature equivalence is a well-known phenomenon in time-dependent material response, where rapid events at a moderate temperature are indistinguishable from some occurring at modest rates but elevated temperatures. However, there is as-yet little elucidation of how well this equivalence holds for substantial plastic strains. In this work, we demonstrate time-temperature equivalence over a large range in a previously studied high-density polyethylene formulation (HDPE). At strain-rates exceeding 0.1/s, adiabatic heating confounds the comparison of nominally isothermal material response, apparently violating time-temperature equivalence. Strain-rate jumps can be employed to access the instantaneous true strain rate without heating. Adiabatic heating effects were isolated by comparing a locus of isothermal instantaneous flow stress measurements from strain-rate jumps up to 1/s with the predicted equivalent states at 0.01/s and 0.001/s in compression. Excellent agreement between the isothermal jump condition locus and the quasi-static tests was observed up to 50% strain, yielding one effective isothermal plastic response for each material for a given time-temperature equivalent state. These results imply that time-temperature equivalence can be effectively used to predict the deformation response of polymers during extreme mechanical events (large strain and high strain-rate) from measurements taken at reduced temperatures and nominal strain-rates in the laboratory.

INTRODUCTION

Time-temperature equivalence is a widely recognized property of many time-dependent material systems, where there is a clear predictive link relating the deformation response at a nominal temperature and a high strain-rate to an equivalent response (i.e., stiffness or flow stress) at a depressed temperature and nominal strain-rate. This is often attributed, in metals and polymers alike, to the deformation response being governed by a local activation process which is a function of the temperature, the applied stress, and the activation energy for the particular activated process, due to Eyring [1, 2]. In metals, the time-temperature equivalent state has been widely related using activation models that are adaptations of the Eyring approach, for example, Zener and Holloman [3], and Zerilli and Armstrong [4, 5]. There have been numerous modeling attempts to capture time-temperature equivalence in polymers, and perhaps the most well-known is the Williams-Landel-Ferry (WLF) formula, which has been extremely successful for predicting small-strain deformations for a moderate window of temperatures in a variety of amorphous polymers [6]. Furthermore, such studies of viscoelasticity are typically confined to the small-strain regime, whether the intended application is time-temperature equivalence or creep modeling, which is problematic for the prediction of large deformations using equivalency approaches. Notably, Zerilli and Armstrong applied their adaptation of the Eyring equation obtained from their work in plasticity of metals to activated flow in polymers [7].

Recent work has investigated time-temperature equivalence in a number of polymers substantially beyond the small-strain regime. Siviour and coworkers examined uniaxial deformations at a wide range of temperatures and strain-rates in polycarbonate, and polyvinyl-difluoride (PVDF), and proposed an empirical linear formula for relating these that agreed well with the data (Figure 1) [8, 9].

$$T_{Eq} = T_{Test} + A[\text{Log}_{10}(\dot{\epsilon}_{Eq}) - \text{Log}_{10}(\dot{\epsilon}_{Test})] \quad (1)$$

This model has a single free parameter (A), here termed the temperature/strain-rate equivalence parameter, which relates the temperature and strain-rate sensitivities of the stress state. When comparing measurements of the yield strength, their results showed that with a single free parameter in the model virtually all experimentally accessible states in temperature and strain-

rate collapsed to a single trend in a given polymer. The agreement was even more remarkable when the test matrix spanned a glass transition, and a sharp inflection was observed in the temperature dependence of the yield strength, and the model nevertheless fit the data at temperatures both above and below the glass transition with a single value for the model equivalence parameter.

Brown and coworkers examined time-temperature equivalence in PTFE, PCTFE, and reported similar agreement with the formula employed by Siviour [10]. In another study, the finite strain time-temperature equivalence behavior of high density polyethylene (HDPE) and ultrahigh molecular weight polyethylene (UHMWPE) were studied and found to agree considerably with one another. It was also found that the temperature dependence of the yield strength exhibited no inflection over a large range of temperatures, in contrast to other polymers so investigated [11]. Their work reported the time-temperature equivalence of the yield strength, as defined as the onset of plasticity, which was observed to occur at 7.5% strain. An important finding of their work showed that one decade of increased strain-rate in that HDPE formulation was equivalent to a 10.2 K reduction in temperature. It is also important to note that their results also revealed substantial adiabatic heating and softening of the materials at strain-rates above 0.1/s. This work also tracked the time-temperature equivalence of the flow stress at 20% strain, $\sigma_{20\%}$, corresponding to the onset of fully-developed plasticity, for a wide range of temperatures and applied true strain-rates. The deformation response for HDPE at these conditions (Figure 1a-b), can be represented directly as the temperature and strain-rate dependence of $\sigma_{20\%}$ can be represented (Figure 1c-d) and they collapse to one equivalent response when Eq.1 is applied with $A=10.2$ K/Decade (Figure 1e).

Fig. 1. (a) Stress-strain response of HDPE with varied temperature and (b) strain-rate. (c-d) Flow stress at 20% strain from (a-b) respectively. (e) Eq. 1. applied to collapse (c-d) to a single equivalent response locus. After [12].

Special attention is paid to $\sigma_{20\%}$ here because the deformation beyond 15% strain in monotonic loading is apparently pure plastic deformation, as the recoverable viscoelastic deformation is exhausted at that point and does not contribute to further deformation [13]. At intermediate strains where both recoverable and plastic deformation are active, the two mechanisms are confounded and could have distinct activation energies and time-temperature equivalence behaviors.

While the wide agreement of time-temperature equivalence in a number of disparate polymers with a single-parameter empirical model is remarkable, one limitation of that work is that only a single locus of stress at a particular strain is used to generate the equivalency. That is, there is no direct reporting of the correspondence of the full deformation response, i.e., the collapsing of the full stress-strain curves of multiple distinct equivalent states. A verification of the correspondence of the entire response is critical to the proper thermomechanical constitutive modeling of the material. From a more pragmatic point of view, point-by-point correspondence over the entire deformation response is necessary if equivalent controlled laboratory-generated stress-strain curves are to be used in place of measurements made at extreme equivalent states that are experimentally inaccessible. In the present work, time-temperature equivalence of the same HDPE studied by Brown and coworkers [11] is extended to the continuous stress-strain curve in compression, beyond yield and beyond 50% logarithmic strain, where the reliability of compression tests becomes tenuous.

Another potential limitation to time-temperature equivalence lies in the difficulty in maintaining a constant specimen temperature at elevated strain-rates. The conversion of plastic work to heat during deformation is well-documented, where

the fraction of the plastic work converted to heat often exceeds 90% [13, 14]. The temperature rise in a specimen during a test is determined by the total plastic work done, the effective thermal plastic work conversion factor ($\beta_{(\epsilon)}$), and the heat capacity, C_p (Eq.2).

$$\Delta T = \frac{\int \beta_{(\epsilon)} \sigma d\epsilon_p}{c_p} \quad (2)$$

When the test is sufficiently rapid heat transfer cannot dissipate the thermal load from plastic work and the test is adiabatic. In this case heat energy cannot escape the specimen during the test and the effective β is maximized. The resulting flow stress follows the deformation response for the instantaneous temperature in the specimen, which manifests as thermal softening (Figure 2).

Fig. 2 Isothermal stress-strain curves for polyethylene for a range of temperatures (red) are qualitatively similar. Specimen temperature rises (ΔT) due to accumulated plastic work converted into heat, dependent on the heat capacity (C_p) and the effective strain-dependent thermal plastic work conversion factor (β). If the test is rapid enough to effectively prevent heat conduction, then the test is adiabatic and the maximum specimen heating takes place. In this case, (a, blue) the observed flow stress follows the isothermal stress-strain for the current specimen temperature. (b) The resulting stress-strain curve in the adiabatic case is qualitatively different than the isothermal curve in the same ambient conditions.

Non-isothermal stress-strain curves are not unique, and therefore have limited interpretability for material characterization. Adiabatic heating therefore frustrates attempts to study time-temperature equivalence between non-isothermal states. Haward and coworkers investigated adiabatic heating in large tensile deformations in HDPE, and found the plastic work at large strains to be nearly completely converted to heat, i.e., $\beta \sim 1$ [13]. Other work has found the conversion to heat of inelastic strains below 10% in polymers to be considerably less complete, owing to the reversibility of the strain through viscoelastic recovery [15-17]. However, the potential effect of adiabatic heating at small or intermediate strains has a diminishing effect on the overall deformation response, as the overall strain energy is still limited at those strains. Thus, while the specimen geometry plays a role in heat dissipation, plastic work heating generally needs to be considered at strain-rates exceeding 0.01/s and strains in excess of 15%.

In the present work, the confounding effect of adiabatic heating on the presumed test temperature was accounted for at large strains by employing sudden strain-rate jumps to access an instantaneous value of the flow stress for elevated strain-rates at a given jump strain, which is therefore obtained prior to measurable adiabatic heating from further plastic work (Figure 3).

Fig. 3 (a) Strain program for constant strain-rate compression testing (solid) and rate-jumps from the lower bound to the upper bound strain-rate. (b) The expected result for ideal viscoplastic behavior, where the response after the strain-rate jump is indistinguishable from the isothermal response at that strain-rate. All responses are drawn in (b) here with the ideal isothermal response, i.e., without specimen heating from plastic work. (c) Adiabatic heating progressively lowers the flow stress after an increment of plastic work has been done, leaving the initial portion of the rate jump response in agreement with the isothermal response at that rate. The corresponding experimental data are then in the form of the isothermal locus of points on the jump response just prior to specimen softening.

Several of these rate-jump measurements were then synthesized to form a locus of the isothermal plastic deformation response (Figure 3c) up to large compressive strains at a constant supplied temperature and elevated (nominally adiabatic) strain-rate. Thus, multiple equivalent states resulting in an identical flow stress at an arbitrary strain can be directly compared though a construction of an experiment with a suitable interchanging of test temperature and strain-rate via the equivalence relation (Eq.1, Figure 4).

Fig. 4 Flow stress dependence on absolute temperature, with multiple strain-rates shown obeying the time-temperature equivalence in Eq.1. Data are represented by the flow stress at a given state, often at a certain strain (e.g., 20%). To check for equivalence from the prediction of Eq.1, multiple tests are run at strain-rate/temperature states that are predicted to exhibit the same flow stress. For strain-rates greater than 0.01 s^{-1} , isothermal conditions are not guaranteed, and specimen heating can confound the comparison, unless strain-rate jump tests are employed.

The purpose of the present work is to identify whether the empirical time-temperature formula (Eq.1) employed point-wise in the literature is sufficient to enable prediction of the full isothermal stress-strain response at large strains and high strain-rates in HDPE from equivalent quasi-static tests at suitably depressed temperatures. Further, this comparison was undertaken over a wide range of temperatures to ensure that a single model fit is suitable for all equivalent temperature/strain-rate conditions of interest.

MATERIALS AND METHODS

Compression tests were conducted with cylindrical specimens 6.2 mm in diameter and height on an MTS 880 servohydraulic load frame (MTS, Eden Prairie MN). The test specimens were machined from the same original stock employed in previous work by the authors [11]. All specimens were measured with a micrometer prior to testing. The specimens were preloaded in load control at 20 N. The tests were conducted in strain control at a computed true strain rate, and the strain was measured by an extensometer during the test mounted directly on the compression stage. Load, displacement, and strain were recorded both at regular time increments and at displacement increments of 0.001 mm. Data were computed as true stress and strain assuming uniform incompressible deformation.

The test temperature was controlled through compression platens cooled by nitrogen exhaust from a liquid nitrogen filled Dewar, and the temperature was controlled within ± 0.5 K of the target temperature through manual adjustment of the gas flow rate. The specimens were loaded between optically flat tungsten carbide platens and were unlubricated. The lateral surfaces of the specimen were insulated from the environment with a foam sleeve. Temperature equilibrium was achieved by delaying testing until the displacement rate under a constant preload of 50 N was negligible ($< 1 \mu\text{m}/\text{min}$). The temperatures employed during testing were 20 C and -50C for a maximum strain-rate of 1/s; test temperature was 20 K or 30 K depressed for comparison isothermal quasi-static conditions at strain-rates of 0.01/s and 0.001/s, respectively. A limited number of quasi-static tests were also conducted below -100 C on the cold platens. Additionally, quasi-static tests were conducted immersed in a liquid nitrogen bath to challenge the modeled linearity of the temperature dependence of the strength at extremely low temperatures.

The tests employed strain-rates of 0.01/s and 0.001/s for baseline isothermal quasi-static conditions (with the latter 10 K cooler in each temperature condition) (Figure 3, 4). Lower strain-rates are impractical for the manual temperature control scheme employed and added little insight to the experiment. A comparison of the deformation response between these two presumably equivalent quasi-static conditions was used as an additional test for isothermality in these tests, as a rate-dependent thermal softening would present as a divergence in the plastic hardening. To assess higher rate isothermal conditions, strain-rate jumps from 0.01 up to a 1/s were conducted, at strains of 10%, 20%, 30%, and 40% (Figure 3a). The maximum strain-rate in a test was held until a true strain of 100 % was achieved to prevent machine deceleration from affecting the data at strains less than 50%. Care was taken to tune the load frame response to ensure that the strain-rate jump occurred with negligible acceleration lag or error, which required the use of a 6 GPM servohydraulic valve in the system.

RESULTS

Using the time-temperature equivalence relation noted above (Eq.1) and the equivalence parameter found from previous work for each material (10.2 K/decade strain-rate), quasi-static near-equivalent conditions for both materials can be directly compared to the results of the rate-jump tests by depressing the temperature by 20 K or 30K for constant true strain-rates of 0.01/s and 0.001/s, respectively (Figure 4). A direct comparison of these quasi-static equivalent states and the rate-jump loci shows generally good agreement for strains exceeding 10%. Thus, by isolating adiabatic heating from the large strain deformation response through the use of strain-rate jumps, excellent agreement is obtained between the isothermal quasi-static equivalent state and the isothermal rate-jump flow stress locus at 1/s without apparent overshooting or undershooting of the isothermal response. Overshoot or undershoot of the jump condition (under isothermal conditions) has been identified as evidence of history dependence of the process, effectively breaking the presumption of general time-temperature equivalence.

At 20 C, the deformation response in HDPE underwent thermal softening at a strain-rate of 1/s; the flow stress was depressed by 3-5 MPa between 20% and 50% strain (Figure 5a). The agreement between the equivalent quasi-static tests is good. The jump locus also agrees well with the quasi-static isothermal equivalent states. The response at -50 C in HDPE exhibits considerable softening, with the flow stress dropping approximately 10 MPa after each rate jump (Figure 5b). The 1/s response softens to the point that the flow stress is lower at large strains than that at 0.01/s -- a hallmark of adiabatic heating effects (Figure 3c).

Fig. 5 Deformation response of HDPE at a nominal temperature of (a) 20°C and (b) -50°C, including strain-rate jumps from 0.01s^{-1} to 1s^{-1} . In green are the predicted isothermal states equivalent to the nominal temperature at 1s^{-1} , with strain-rates of 0.01s^{-1} and 0.001s^{-1} . Good agreement between the equivalent states and the isothermal jump locus is obtained.

To test for increased temperature sensitivity of the flow stress below -80 C, quasi-static tests were conducted at further reduced temperatures, including immersion in liquid nitrogen (Figure 6). The temperature dependence of the strength is clearly non-linear when taken to low temperatures, with the deviation occurring around -90 C (180 K).

Fig. 6 The flow stress in HDPE at 20% strain is exponential with absolute temperature with a high degree of correlation for temperatures substantially below the melting temperature (410 K). However, there is apparently a breakdown in the exponential fit above room temperature (293 K) where the flow stress decreases linearly and drops to zero near the melt temperature. Note that for temperatures between 200 K ($T_m/2$) and 300 K, a linear relation is approximate for many applications of interest, though this observation obscures a good interpretation of the overall data.

DISCUSSION

The agreement of the isothermal deformation response at quasi-static and elevated strain-rates in HDPE, over a wide range of plastic strains, extends the applicability of time-temperature equivalence techniques in these materials into the large strain regime. This significantly improves the efficacy of time-temperature equivalence relations by enabling the translation of continuous stress-strain curves obtained in the laboratory at quasi-static isothermal conditions into dynamic regimes of behavior at substantially elevated strain-rates. The ability to shift experimental stress-strain curves is extremely valuable in the development or evaluation of rate-dependent constitutive models, where model predictions of difficult-to-test extreme mechanical conditions (e.g., large strains at high strain-rates) can be directly compared to time-temperature equivalent conditions from laboratory data. Time-temperature equivalence holding over a wide range of strains and temperatures also implies that one mechanism of temperature-dependence is active in general, which is also useful information for model development.

It is also of note that the jump locus coincides directly with the equivalent state, apparently without substantial overshoot or undershoot. In metals, such a disagreement is linked to the pinning or accumulation of dislocations (respectively), making the rate-sensitivity a history dependent phenomenon. The rate-sensitivity in HDPE, and hence its time-temperature equivalence, appears to be history-independent and therefore generally applicable. We had hypothesized that there would be a history dependence in HDPE, as HDPE has thick crystal lamellae that are likely dominated by dislocation half-loops [18] that are likely to interact and perhaps tangle than pure screw dislocations during dynamic loading, resulting in a path- or history-dependence in plasticity. More work is warranted to elucidate the path-independence of the time-temperature equivalence in polyethylenes, with attention to activation phenomena, while employing more complicated strain histories.

It has been observed in many materials that adiabatic heating effects are exacerbated at depressed temperatures, and the results of this work are consistent with those observations. To hedge against this phenomenon, which could potentially lead to heating even at 0.01/s, equivalent conditions at 0.01/s and 0.001/s both were compared to the isothermal rate-jump locus and to one another. The agreement of both quasi-static strain-rates with the rate-jump locus strengthens the claim of equivalence by collapsing three equivalent states, and clarifies that heating effects do not confound the 0.01/s data above -80C.

The linear strength dependence on temperature implied by the equivalence relation (for log-linear strength – strain-rate dependence) is likely sufficient for most mechanical conditions that could occur in the service of components, as extremely low temperatures correspond to extremely high strain-rates. For instance, for a loading at a depressed temperature of -20 C to be affected by the observed deviation from linearity of the strength, according to the non-linear strength model fit, the strain-rate would have to exceed $10^5/s$. Such a high strain-rate is unlikely to occur in most applications, making the distinction largely academic. However, even if such conditions were a concern, strain-rates substantially exceeding $10^5/s$ the response must also take into account shock wave and compressibility phenomena, and thus a refinement of the model would be

necessary to accurately predict such a deformation. Still, there is an indication that a general non-linear treatment of the temperature dependence of the flow stress could be more consistent and physically motivated than the treatment in the empirical equivalence model employed here and elsewhere.

CONCLUSION

This work demonstrated that the empirical time-temperature equivalence model proposed by Siviour [8, 9] is suitable for the prediction the continuous deformation response of HDPE at elevated strain-rates from quasi-static data at depressed temperatures above -80 C. Further, the effect of adiabatic heating, which was clearly evident at substantially depressed temperature and strain-rates above 0.1/s, was successfully accounted for by assessing the isothermal deformation response at elevated strain-rates by employing strain-rate jumps. Thus, the results of this work enable the predictive translation of quasi-static stress-strain curves into equivalent dynamic mechanical conditions for a wide range of temperatures. Such a translation enables the comparison of advanced constitutive model predictions of dynamic deformation response directly with well-controlled laboratory data (with adiabatic heating taken into account), as experimental measurement of the deformation response at large strains and high strain-rates is typically not feasible. Further work is warranted to clarify large strain time-temperature equivalence for all temperatures in polyethylene and other polymers, with attention to the non-linear dependence of flow stress on temperature and the mechanisms of temperature- and time-dependence implied by such relationships.

REFERENCES

1. Eyring, H., *The activated complex in chemical reactions*. Journal of Chemical Physics, 1935. **3**(2): p. 107-115.
2. Eyring, H., *Viscosity, plasticity, and diffusion as examples of absolute reaction rates*. Journal of Chemical Physics, 1936. **4**(4): p. 283-291.
3. Zener, C. and J.H. Hollomon, *Effect of strain rate upon plastic flow of steel*. Journal of Applied Physics, 1944. **15**(1): p. 22-32.
4. Zerilli, F.J. and R.W. Armstrong, *Dislocation-Mechanics-Based Constitutive Relations for Material Dynamics Calculations*. Journal of Applied Physics, 1987. **61**(5): p. 1816-1825.
5. Zerilli, F.J. and R.W. Armstrong, *The Effect of Dislocation Drag on the Stress-Strain Behavior of Fcc Metals*. Acta Metallurgica Et Materialia, 1992. **40**(8): p. 1803-1808.
6. Williams, M.L., R.F. Landel, and J.D. Ferry, *Mechanical Properties of Substances of High Molecular Weight .19. The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-Forming Liquids*. Journal of the American Chemical Society, 1955. **77**(14): p. 3701-3707.
7. Zerilli, F.J. and R.W. Armstrong, *A constitutive equation for the dynamic deformation behavior of polymers*. Journal of Materials Science, 2007. **42**(12): p. 4562-4574.
8. Siviour, C.R., et al., *The high strain rate compressive behaviour of polycarbonate and polyvinylidene difluoride*. Polymer, 2005. **46**(26): p. 12546-12555.
9. Siviour, C.R., et al., *Mechanical behaviour of polymers at high rates of strain*. Journal De Physique Iv, 2006. **134**: p. 949-955.
10. Brown, E.N., P.J. Rae, and G.T. Gray, *The influence of temperature and strain rate on the tensile and compressive constitutive response of four fluoropolymers*. Journal De Physique Iv, 2006. **134**: p. 935-940.
11. Brown, E.N., et al., *Soft recovery of polytetrafluoroethylene shocked through the crystalline phase II-III transition*. Journal of Applied Physics, 2007. **101**(2).
12. Brown, E.N., et al., *Influence of molecular conformation on the constitutive response of polyethylene: A comparison of HDPE, UHMWPE, and PEX*. Experimental Mechanics, 2007. **47**(3): p. 381-393.
13. Hillmansen, S. and R.N. Haward, *Adiabatic failure in polyethylene*. Polymer, 2001. **42**(22): p. 9301-9312.
14. Hillmansen, S., et al., *The effect of strain rate, temperature, and molecular mass on the tensile deformation of polyethylene*. Polymer Engineering and Science, 2000. **40**(2): p. 481-489.
15. Brooks, N.W., R.A. Duckett, and I.M. Ward, *Investigation into Double Yield Points in Polyethylene*. Polymer, 1992. **33**(9): p. 1872-1880.
16. Salamatina, O.B., et al., *Thermodynamics of inelastic deformation of amorphous and crystalline phases in linear polyethylene*. Polymer Science Series A, 2011. **53**(9): p. 775-786.
17. Shenogin, S.V., G.W.H. Hohne, and E.F. Oleinik, *Thermodynamics of the pre-yield deformation behavior of glassy polymers: measurements with new deformation calorimeter*. Thermochemica Acta, 2002. **391**(1-2): p. 13-23.
18. Argon, A.S., A. Galeski, and T. Kazmierczak, *Rate mechanisms of plasticity in semi-crystalline polyethylene*. Polymer, 2005. **46**(25): p. 11798-11805.