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Mechanical Properties of Plastic-Bonded Explosive Binder Materials as a Function of Strain-Rate and Temperature.

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Abstract. Recently, interest has been shown concerning the mechanical response of plastic-bonded explosives (PBX) to enable the development of predictive materials models describing the mechanical behavior of these composites. Accordingly, detailed information about the constituents is crucial. Compression measurements were conducted on two explosive formulation binders, extruded Estane™ and Estane™ with nitroplasticizer, as a function of temperature from -55°C to +25°C using a specially-designed split Hopkinson pressure bar (= 3500 s⁻¹) and quasi-statically (= 0.001 to 1 s⁻¹) using a hydraulic load frame. The mechanical response of the Estane™ binder was found to exhibit higher flow strengths and strain rates and temperature dependency than the Estane™ binder with nitroplasticizer. The visco-elastic recovery of the binders is seen to dominate the mechanical behavior at temperatures above the glass transition temperature (Tg). Both binders exhibited increasing elastic loading moduli, E, with increasing strain rate or decreasing temperature, which is similar to other polymeric materials. Also, the Tg shifts to higher temperatures as the strain rate is increased. The binders are shown to be sensitive to strain rate and temperature below Tg. The binders exhibit a yield behavior, followed by an increasing maximum flow stress, σ⁰, or the strain-at-maximum stress, ε⁰, which occurs when the binder first yields for increasing strain rate or decreasing temperature. A discussion of the Hopkinson bar technique as applied to polymeric or low impedance materials is described in detail.

INTRODUCTION

It is well known that increasing the strain-rate strongly effects the mechanical response of polymers in tension[1-3] and compression[4-6]. Increasing the strain rate leads to higher modulus because the polymer chains have less chance to flow. Understanding and modeling the mechanical response of polymers and polymer-based composites is of great interest for defense and commercial applications related to: 1) the need for predictive constitutive model descriptions for use in large-scale finite-element simulations of damage and deformation, and 2) focused emphasis on understanding the dynamics of localization phenomena and mechanical failure of polymeric composites. New continuum models, based on actual physical and chemical mechanisms, to describe complex loading processes must account for complex phenomenology including temperature, strain rate, orientation, and aging effects on mechanical performance if a predictive capability is to be achieved.

Conventional methods have been used to measure the mechanical properties of polymers and polymer composites at low strain rates. However, high strain rate methods using the split Hopkinson pressure bar (SHPB) must be modified for these materials to achieve stress equilibrium with low sound speed materials; obtain adequate pressure bar signal output at very low stress levels; and minimize undesirable
stress triaxiality caused by friction on specimen interfaces. Recent studies by the authors [5-7] have shown how to minimize these issues by optimizing specimen geometry, through the use of low modulus pressure bars, and by using lubricants effective over a wide range of temperatures. Predicting the constitutive behavior of these composite materials requires that the constituents be well understood and that physically based models can be developed to predict their behavior. The compressive constitutive responses of a number of polymers and plastic-bonded explosives (PBX) have been studied as a function of strain rate and temperature [5-11]. Beginning with the high-rate Hopkinson split-bar studies of Hoge[8] on a range of PBXS and continuing with the high-strain rate work of Palmer[9], Dion [4], Xia [10], and Gray [5-7] it has been found that: a) the effective elastic modulus of polymers and polymer composites are strongly influenced by strain rate and temperature, b) polymers below the glass transition temperature continue straining after the maximum flow stress has been achieved, i.e. viscoelastic-plastic behavior is indicated, and c) sample-size and lubrication effects are critical due to the very slow stress wave propagation through polymers and polymer composites. In general, the compressive strength and the loading modulus of polymeric materials increases with decreasing temperature and increasing strain rate.

In the present investigation, uniaxial compression tests were performed at quasi-static and high-strain rates for temperatures from −55°C to +25°C on extruded Estane™ and Estane™ with nitroplasticizer. Results illustrating the effect of composition, temperature and strain rate on the constitutive response of the polymers will be presented.

**EXPERIMENTAL TECHNIQUES**

**Materials and Preparation**

The first of the two polymers examined in this study was Estane 5703 (segmented poly(ester urethane)). It was obtained in pellet form from The BF Goodrich Co. Estane 5703 contains approximately 25% hard segments which are composed of 4,4i-methylenediphenyl 1,1i-diisocyanate (MDI) and a 1,4 butanediol chain extender. The soft segments are comprised of poly(butylene adipate). The glass transition temperature (Tg) of Estane is −31°C, a melting temperature of ~105°C, and an ambient specific gravity of 2.0 g/cm³.[11] The bulky copolymer backbone is composed of soft and hard segments that enhance entanglement. Estane™ is known for its resistance to hydrocarbon and solvent attack, low temperature flexibility, high temperature resistance, and good adhesive properties. The high strength of the copolymer is associated with its ‘virtual crosslinking’ attributed to both molecular entanglement and intermolecular forces (i.e. hydrogen bonding, van der Waals, and polar attraction) concentrated at the ester linkages.

The other polymer binder examined in this study was Estane 5703 (49 wt%) / a eutectic mixture of bis(2,2-dinitropropyl) acetal and bis(2,2-dinitropropyl)formal [abbreviated BDNPA-F] (49 wt%) / and a free radical inhibitor (either diphenylamine (DPA) or Irganox 1010)(2 wt%). The polymer binder was also processed in the same way as above in billet form, from which the experimental samples were machined. The binder material chosen for this study contained the Irganox free radical inhibitor. The addition of the BDNPA-F plasticizer lowers the static glass transition temperature to −40°C and causes the polymer strength to decrease, but the toughness and flexibility are increased. The addition of plasticizer to the Estane™ acts as a ‘lubricant’ to promote the sliding of the polymer chains, and to reduce the degree of entanglement.

Cylindrical compression specimens 6.35 mm in diameter and either 6.35 mm or 3.15 mm in length (L/D of 1 or 0.5) were machined for low and high-strain-rate testing, respectively, from the Estane™ and the Estane™, with “nitroplasticizer” starting billets. Due to the soft, visco-elastic nature of the polymers at ambient temperatures, a liquid nitrogen cooling procedure was employed to machine specimens with parallel loading surfaces.

**Low Strain Rate Compression Testing**

Quasi-static and low-strain-rate compression tests were conducted at strain rates of 0.001, 0.1 and 1 s⁻¹ at temperatures from −55°C to 25°C. The compression tests were conducted with an MTS model 880 test frame with a liquid nitrogen cooled cold stage. The cold stage cools the samples by controlling the volume of gas passing through the loading platens. Tests were run in displacement control and the specimen strain was quantified using a displacement extensometer. Specimens were
loaded to plastic strains of ~30% then unloaded. Samples were lubricated using either a thin layer of molybdenum disulfide grease, molybdenum disulfide spray lubricant, or boron nitride spray lubricant for cold temperature applications and tested in laboratory air with a relative humidity of ~15±4%.

High Strain Rate Compression Testing

Dynamic tests were conducted as a function of strain rate, ~3500 s\(^{-1}\), and temperature, -55°C to +25°C, utilizing a modified split-Hopkinson pressure bar (SHPB)[5-7]. The SHPB used for this study was equipped with either 9.4-mm diameter Ti-6Al-4V or Magnesium AZ31B-alloy bars that improve the signal-to-noise level needed to test extremely low strength materials as compared to the maraging steel bars traditionally utilized for SHPB studies on metals. The lower sound speed titanium and magnesium bars also help achieve sample stress equilibrium sooner, but because of the inherent oscillations in the dynamic stress-strain curves and the lack of stress equilibrium during initial load-up, the determination of yield strength must be considered inaccurate, at best, at high strain rates.

Controlled temperature variations between -55°C to +25°C were achieved using a specially-designed gas manifold system developed at the Los Alamos National Laboratory (LANL) where samples were cooled and heated using helium (He) gas within a 304-stainless steel containment chamber held at a partial vacuum. The He gas is cooled below ambient temperature by first passing the He through a copper coil positioned within a liquid nitrogen dewar. Specimens were ramped to the desired temperature in approximately 5 minutes and equilibrated at temperature for approximately 10 minutes prior to testing. SHPB samples were lubricated with either a thin spray coating of boron nitride or a thin layer of molybdenum disulfide grease.

The inherent oscillations in the dynamic stress-strain curves and the lack of stress equilibrium in the specimens at low strains make the determination of yield strength inaccurate at high strain rates.

RESULTS AND DISCUSSION

The compressive true-stress versus true-strain response of the explosive binders were found to depend on the applied strain rate, varied between 0.001 and 3000 s\(^{-1}\), and the test temperature, varied between -55°C and 23°C. The compressive(visco-elastic) stress-strain response of Estane™ is shown in Fig. 1 for several strain rates and temperatures. The loading modulus of this binder at 23°C increases from ~3.33 MPa at 0.001 s\(^{-1}\) to 6.7 MPa at 1 s\(^{-1}\) to ~21 MPa at a strain rate of 2400 s\(^{-1}\), an ~6-fold increase in apparent loading modulus. The increase in strength of the Estane™ at 23°C (at 10°/0 strain) was a factor of 7 from 0.44 MPa at 0.001 s\(^{-1}\) to 3.1 MPa at 2400 s\(^{-1}\). The constitutive response of the Estane™ with nitroplasticizer (1:1 Estane /
BDNPA-F) was similarly studied quasi-statically and at high strain rate as shown in Figure 2. The loading modulus of this binder at 23°C increases from -0.46 MPa at 0.001 s⁻¹ to 1.35 MPa at 1 s⁻¹ to -3.27 MPa at a strain rate of 2200 s⁻¹, an ~7-fold increase in apparent loading modulus. The increase in strength of the Estane™ with nitroplasticizer at 23°C (at 10% strain) was measured to be a factor of ~15 from 0.05 MPa at 0.001 s⁻¹ to 0.77 MPa at 2200 s⁻¹. An understanding of the influence of temperature and strain rate on individual constituents of PBX composites, such as energetics and propellants, is needed to support robust constitutive-model development on a range of PBX formulations. The stress-strain data measured in this study demonstrates: 1) the low overall flow strength of these binders above the glass transition temperature, 2) the order of magnitude increase in the binder flow stress when the test temperature is lowered from ambient to -20°C at high-strain rate, and 3) the equally large increase in the binder flow strength associated with increasing the strain rate.

**Validity of SHPB Testing of Polymers**

Due to the documented dispersive nature of wave propagation in ductile polymers and the potential influence of sample size on attaining a uniform stress state, the high-rate constitutive response of Estane™ was carefully probed to obtain well-posed and accurate data[5-7].

To assure valid high-rate measurements on Estane™, it is instructive to examine the different analyses[9] used to calculate sample stress from the Hopkinson bar strain as shown in Figure 2. In the 1-wave analysis the sample stress is directly proportional to the bar strain measured from the transmitted bar. The 1-wave stress analysis reflects the conditions at the sample-transmitted bar interface and is often referred to as the sample “back stress”. This analysis results in more accurate and smoother stress-strain curves, especially near the yield point. Alternatively in a 2-wave analysis, the sum of the synchronized incident and reflected bar waveforms (which are opposite in sign) is proportional to the

![Nitroplasticized Estane Low Strain Rates and Temperature Results](image1)

**FIGURE 2.** True stress-strain data for Estane™ with nitroplasticizer (1:1 Estane / BDNPA-F) for several temperatures and strain rates.
sample "front stress" and reflects the conditions at the incident/reflected bar-sample interface.

Finally a third stress-calculation variation that considers the complete set of three measured bar waveforms, the 3-wave analysis, is simply the average of the 2-wave "front" and the 1-wave "back" stress. A valid, uniaxial Hopkinson bar test requires that the stress state throughout the sample achieve equilibrium during the test and this condition can be checked readily by comparing the 1-wave and 2-wave (or 3-wave) stress-strain response. When the stress state is uniform throughout the sample, then the 2-wave stress oscillates about the 1-wave stress, as seen in Figure 3. Additionally, relatively constant strain rates are also required for a valid SHPB test. For the current study on Estane™ and Estane™ with nitroplasticizer only tests meeting these criterion were deemed acceptable. Previous Hopkinson-bar studies of ceramic materials using this 1-wave versus 3-wave comparison have shown quite dramatically that a sample is not in stress equilibrium when divergence is observed. In ceramic and cermet materials this divergence correlates very well with the onset of non-uniform plastic flow and/or fracture events before stress equilibrium is achieved.

Attainment of stress state equilibrium at high-strain rates for the polymers investigated in this study was also found to be dependent on the test temperature. Specifically, at low test temperatures polymer specimens equilibrate more quickly because their stiffness (i.e. elastic modulus and sound speed) increases significantly. Accordingly, the "worse-case" condition for the evaluation of SHPB specimen L/D = 0.5 is at high temperatures. Viscoelastic

![Graph](image)

**FIGURE 3:** Stress-strain response of Estane at 0°C, a) showing 1- and 2-wave stress curves in addition to the strain rate.
effects are pronounced in the Estane™ with nitroplasticizer at 23°C, and approximately 2% strain is needed before stress-state equilibrium is achieved. Through comparisons of this type, it was determined that a specimen aspect ratio of L/D=0.5 is optimum for achieving valid test data for the binders studied. Only tests meeting all of the criteria discussed were deemed valid.

Although it is observed in both binders that the $T_g$ shifts to higher temperatures as the strain rate is increased, the apparent yield strain was found to be consistently in excess of 5% strain for the pure Estane™ but it reached the apparent yield strain for the Estane™ with nitroplasticizer at a much lower strain (< 1.5% strain). The data on these binders are consistent with the pronounced influence of strain rate and temperature on the mechanical behavior for other ductile polymers. Coincident with a flow stress increase upon decreasing the temperature is an increase in the apparent loading modulus with decreasing temperature. At high strain rates, the magnitude of the increase is >70 times from room temperature to -40°C, from 22 MPa to 1.5 GPa as seen in Estane™ and greater than a 500 fold increase from 3.25 MPa to ~2.0 GPa as seen in the Estane™ with nitroplasticizer. Of course ~40°C is below the dynamic glass transition ($T_g$) for both polymers.

Figure 4 is a summary plot of strength (stress at 10% strain) versus test temperature for the materials and conditions studied. As expected, the Estane™ with nitroplasticizer was softer. It is also noted that below the glass transition there is a seemingly linearly decreasing temperature dependency at all strain rates. High strain rate loading increases the glass transition temperature and also increases dependence (slope) of the flow stress.

**FIGURE 4.** Temperature dependence of the compression strength of the binder and composites as a function of strain rate and vol. %. The maximum of peak stress or stress at 10 % strain was used in this plot.
SUMMARY AND CONCLUSIONS

The following conclusions can be drawn: 1) the compressive stress-strain response of both PBX binders, Estane™ and Estane™ with nitroplasticizer, were characterized to be strongly dependent on both strain rate and temperature, with the modified Estane™ being more sensitive to both variables; 2) decreasing the temperature at high strain rate was found to increase the maximum flow strengths, the apparent loading modulus, and the strain-at-maximum-stress of both the Estane™ and the Estane™ with nitroplasticizer; and 3) Measurement of the constituents of the PBX composites is clearly necessary for the development of proper constitutive behavior and failure m models.

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