

QUASI-STATIC AND DYNAMIC MECHANICAL PROPERTIES OF NEW AND VIRTUALLY-AGED PBX 9501 COMPOSITES AS A FUNCTION OF TEMPERATURE AND STRAIN RATE

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PBX 9501 contains ~95 wt% HMX and 5 wt% binder system comprised of a 1:1 mixture of Estane®5703 and a nitroplasticizer (NP). Prior studies have shown that storage of PBX 9501 in humid environments leads to hydrolysis of the ester linkages in the Estane that reduces its molecular weight. In addition, some nitroplasticizer has been shown to migrate out of the formulation with time. Four lots of PBX 9501 were formulated using new Estane and *virtually-aged* Estane which had been exposed to 70°C and 74% relative humidity for 14, 23 and 36 days. To mimic extreme NP migration, two lots of X-0557 were formulated similar to PBX 9501 but with reduced NP/Estane ratios in the binder. Quasi-static and dynamic (split-Hopkinson pressure bar (SHPB)) compression tests were conducted, in addition to quasi-static tension tests, at temperatures between -55 to 50°C. The dynamic compression data show significant differences between the baseline and VA Estane specimens *only* at -15°C; however, significant differences are observed in the quasi-static compression data at all three temperatures. Reduced NP content strongly increases the strength and modulus of X-0557 versus PBX 9501.

INTRODUCTION

Plastic-bonded explosives (PBXs) are used in a variety of conventional and nuclear defense applications. These materials are engineered to provide reliable performance and maximum safety envelopes. Predictive computational methods have been developed and applied to assure weapons systems reliability under potential accident scenarios. In addition, models are being developed to include and predict the effects of long-term storage and aging on energetics and weapons components. These theoretical efforts rely on many different types of PBX

measurements and experiments for model verification and validation.

Due to their highly-filled composite nature, PBX materials exhibit complex physical and mechanical properties that are dependent on a number of variables, e.g. storage/test temperature, humidity, strain rate, density, formulation, composition, polymer molecular weight, confining pressure, and size distribution of solids, etc.¹⁻⁵

PBX 9501 is an HMX-based composite comprised of ~95 weight percent (wt%) HMX, ~5 wt% binder, and ~0.1 wt% stabilizer. The binder is a 1:1 mixture of Estane®5703 (Estane), a polyester

polyurethane block co-polymer, and a eutectic mix of bis(2,2-dinitropropyl)acetal - formal [BDNPA-F] (hereafter referred to as nitroplasticizer, NP). Long-term exposure to a humid environment decreases the molecular weight (MW) of the Estane elastomer as the polyester portions of the chains are particularly susceptible to acid-catalyzed hydrolysis.⁶ A second aspect of PBX 9501 aging involves the NP, a volatile constituent that can migrate out of the composite, particularly at elevated temperatures or when in contact with other materials that can readily absorb plasticizer.

This paper reports results of an experimental study characterizing mechanical property changes due to compositional variations believed to be relevant to the aging of PBX 9501, as a function of temperature and strain rate. Quasi-static (low strain rate, tension and compression) and dynamic (high strain rate, compression) data are presented for PBX 9501-like composites in which (1) the Estane MW was reduced prior to formulation, or (2) the formulated NP wt% was decreased from nominal.

EXPERIMENTAL

Materials

The baseline PBX 9501 was formulated in 1999 using pelletized Estane. Estane from the same lot was *virtually-aged* (VA) by exposure to 70°C and 74% relative humidity for 14, 23 and 36 days. This material was used to formulate 3 lots of VA PBX 9501. The Estane weight-averaged molecular weight, M_w , was then measured using gel permeation chromatography (GPC) with tetrahydrofuran (THF) as the solvent, using a polystyrene standard. The M_w values were measured as 115, 88.9,

72.1 and 44.9 kDaltons for the 0-, 14-, 23- and 36-day VA Estane, respectively.

Two X-0557 lots were formulated to represent a drastic migration of NP from the composite system. Compositions for the baseline and VA PBX 9501 formulations and the two X-0557 lots (Lot 7287 and Blend 99-02) are listed in Table 1 with the average specimen density obtained using immersion methods, and the glass transition temperature, T_g , measured¹⁰ by modulated differential scanning calorimetry (MDSC) at 2°C/min. Composition and immersion analyses show that Blend 99-02 has an NP/Estane ratio of 0.38, and Lot 7287 has an NP/Estane ratio of 0.27 with increased fractions of HMX and Estane, and higher pressed densities relative to PBX 9501.

Low Strain Rate Compression and Tension Testing

Quasi-static tension and compression tests were performed on an Instron 5567 Workstation equipped with a Bemco environmental chamber. In compression, two contact extensometers were mounted with knife-edges in contact with the specimen circumference, 180° apart. In tension, only one extensometer was used. The Bemco chamber temperature was ramped at ~1°C/min to the final temperature and held for ~20 minutes prior to testing. The chamber temperature is accurate to $\pm 0.5^\circ\text{C}$ and was determined from the average of two thermocouples mounted inside the upper and lower specimen platens. Quasi-static compression cylinders were machined to 9.5mm diameter and 19mm long. Tension specimens were machined to 76.2mm long cylindrical dogbones with

TABLE 1: COMPOSITION AND AVERAGE SPECIMEN DENSITY
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Formulation/HE	HE (wt%)	Binder (wt%)	Average Density (g/cm ³)
0-day PBX 9501 Lot 7278 (T _g =-46.5°C)	94.64 HMX 3:1 ratio of Class1:2	2.58 Estane 5703 2.57 BDNPA-F 0.09 Irganox	1.827 ± .002 (%TMD=98.44)
14-day VA PBX 9501 Lot 7284 (T _g =-46.4°C)	94.85 HMX 3:1 ratio of Class 1: 2	2.54 Estane 5703 2.50 BDNPA-F 0.11 Irganox 1010	1.831 ± .001
23-day VA PBX 9501 Lot 7279 (T _g =-47.9°C)	94.92 HMX 3:1 ratio of Class 1: 2	2.53 Estane 5703 2.57 BDNPA-F 0.09 Irganox 1010	1.829 ± .001
36-day VA PBX 9501 Blend 99-01 (T _g =-48.6°C)	94.96 HMX 3:1 ratio of Class 1: 2	2.44 Estane 5703 2.48 BDNPA-F 0.10 Irganox 1010	1.828 ± .001
X-0557 Blend 99-02 (T _g =-40.4°C)	96.45 HMX 3:1 ratio Class 1:2	2.53 Estane 5703 0.95 BDNPA-F 0.11 Irganox 1010	1.832 ± .002 (%TMD=98.49)
X-0557 Lot 7287 (T _g =-39.3°C)	96.71 HMX 3:1 ratio Class 1:2	2.55 Estane 5703 0.69 BDNPA-F 0.12 Irganox 1010	1.836 ± .002 (%TMD=98.40)

15° tapers flaring to 21.5mm diameter and a 38.1mm gauge length of diameter 12.7mm.

All tests were performed in crosshead speed control (12.7 and 127 mm/min in compression, 25.4 and 254 mm/min in tension), giving nominal strain rates of 0.011 and 0.111 s⁻¹, respectively. In compression, a graphitic molybdenum disulfide lubricant was used on the cylinder ends. No lubrication was used in tension. The tensile grips were fixed to the pull rods and utilized an internal 16.5° taper to engage and load the specimens. Average stress-strain values and standard deviations were calculated from five replicate tests per condition.

High Strain Rate Compression Testing

Dynamic compression cylinders were machined to 6.35mm in diameter by 3.18mm in length. Dynamic tests were

conducted at a strain rate of ~2000 s⁻¹ as a function of temperatures from -15°C to +50°C, utilizing a split-Hopkinson pressure bar (SHPB) equipped with Ti-6Al-4V pressure bars.⁷

The SHPB used a helium gas manifold system⁷ to cool and heat specimens within a 304-stainless steel containment chamber under a partial vacuum. Specimens were lubricated using either a thin layer of molybdenum disulfide grease or a boron nitride spray lubricant. Five replicate specimens were tested per test condition.

RESULTS AND DISCUSSION

Three parameters were used to characterize the quasi-static stress-strain curves: maximum stress, σ_m , defined as the highest stress achieved before failure of the material; maximum strain, defined as the

strain value at maximum stress, ϵ_m ; and modulus, E . Ideally, the modulus is the slope of the linear elastic portion of the stress-strain curve. However, the low-strain region is typically affected by an experimental toe artifact,⁸ attributed to spurious displacements accumulated while seating the specimen before uniaxial loading is achieved. Therefore, we define the modulus as the slope of the linear fit to a portion of the stress-strain curve centered nominally at 50% of σ_m (E_{50}). The toe correction is defined as the strain intercept value at zero stress for the E_{50} tangent line. The strain data is shifted by the toe correction value to pass the tangent line through the origin and the value of ϵ_m can then be accurately determined.

PBX 9501 and VA PBX 9501

Figures 1 and 2 show the quasi-static tension and compression parameters, respectively, for PBX 9501 and VA PBX 9501 at different temperatures and strain rates, plotted as a function of Estane M_w . These results indicate, in general, that the molecular weight of Estane correlates directly, although rather mildly, with the maximum stress of the material, σ_m . There is a similar, but weaker, trend in the compressive and tensile modulus, E_{50} with M_w , however the data at low temperature are more scattered. One possible reason for this behavior is that low M_w polymers have increased chain mobility and fewer chain

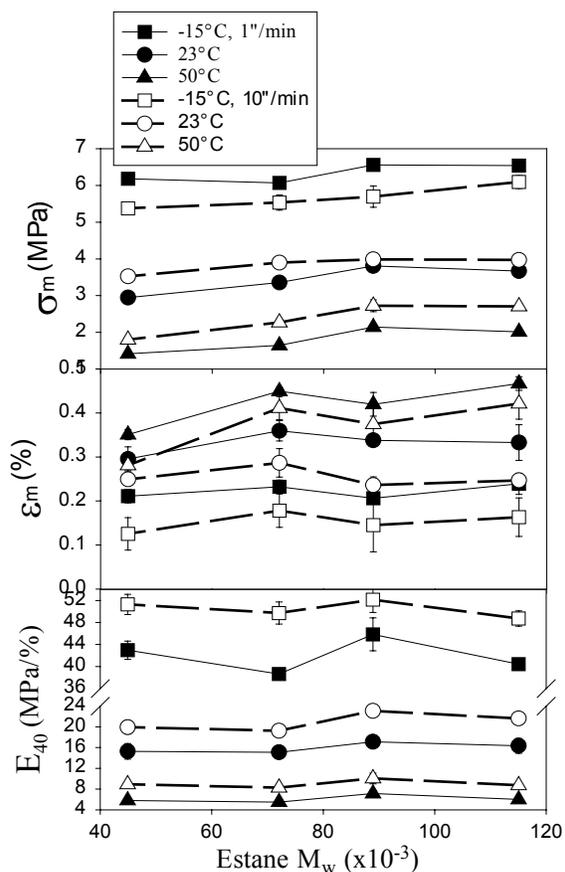


FIGURE 1: QUASI-STATIC TENSION PARAMETERS VS. ESTANE M_w .

entanglements that can decrease the material's toughness, modulus, and strength.

In both tension and compression, ϵ_m values decrease with decreasing M_w , except at the lower temperature in compression where they increase slightly. The tensile trends at 23°C for the PBXs are very similar to observations from ambient tensile data of the pure Estane polymer as a function of Estane M_w ,⁹ except the magnitude of the effect is much greater in pure Estane.

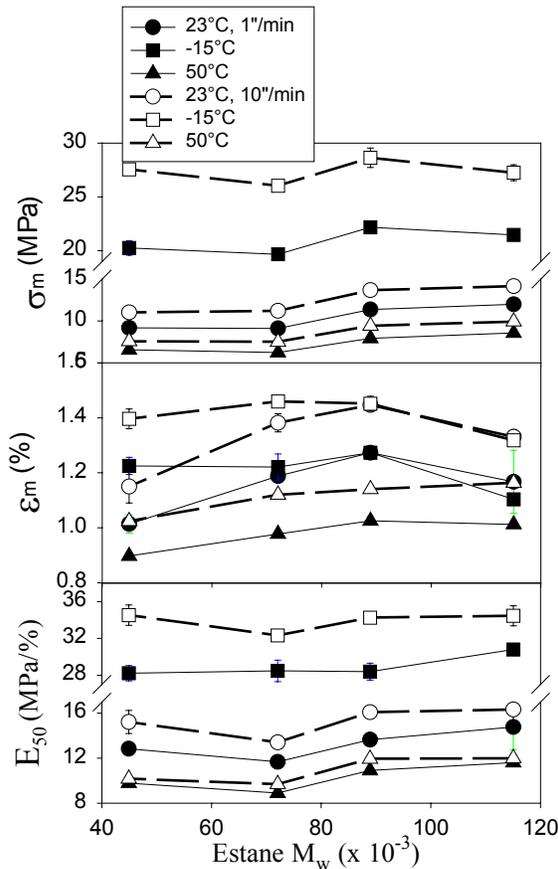


FIGURE 2: QUASI-STATIC COMPRESSION PARAMETERS VS. ESTANE M_w .

For all M_w values in quasi-static tension and compression, a decreased temperature results in an increased strength as the T_g value of the binders (-46.5 to -48.6°C) is approached. For all temperatures and M_w values (excluding tension at -15°C), a higher strain rate results in an increased σ_m . In tension at -15°C and a strain rate of 0.11 s^{-1} , there is an inversion of this trend, indicating a possible change in the deformation mechanism.

For all M_w values, the tensile ϵ_m values increase significantly as the temperature is increased, while the compressive ϵ_m values tend to decrease moderately. Binder

adhesion and elongation play a more significant role in the tensile versus compressive deformation of PBX 9501, and therefore temperature effects are anticipated to be larger in the tensile data. One method to compare tensile and compressive data is to use the ratio of tension to compression modulus E_{50} . The E_{50} ratio at -20°C and 1 in/min drops from ~1.2 to ~0.90 as the M_w drops from 115 to 45 kDaltons. The E_{50} ratio change is similar at -20°C and 10 in/min. The change in the relative magnitude of the E_{50} ratios as a function of M_w provides insight into the different roles of the binder in the two types of loading. At low temperatures relative to the T_g of the binder, the tensile modulus is larger than the compressive modulus. As the binder T_g is lowered by decreasing the M_w relative to the test temperature,¹⁰ the compressive modulus becomes greater than the tensile modulus.

Figure 3 shows the SHPB results for only the 14- and 36-day VA PBX 9501 at ~2000 s^{-1} and -15, 23 and 50°C. Significant changes in the maximum stress as a result of decreasing the molecular weight of Estane were observed at -15°C only. The 0- and 23-day VA PBX 9501 data showed no changes in the stress-strain response. The shape of the -15°C stress-strain curves in Figure 3 shows a rapid drop-off of the flow stress, indicating a more brittle response at lower temperatures.

PBX 9501 and X-0557 (Reduced NP)

Figure 4 shows the tension and compression stress-strain behavior of PBX 9501 and the two X-0557 lots at 23°C and a strain rate of ~0.011 s^{-1} . The tensile strengths are only ~25% of the compressive strengths, and the tensile fracture strains

are only ~20% of the compressive strains at maximum stress.

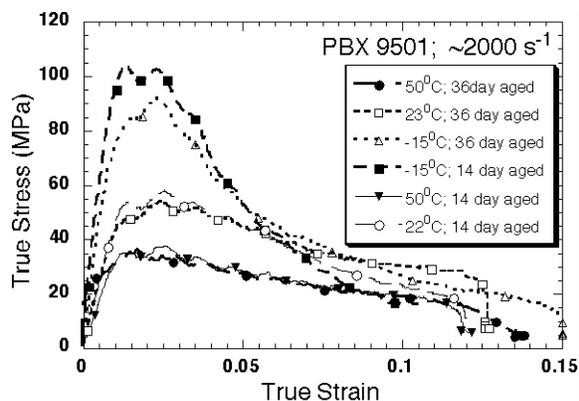


FIGURE 3: SHPB COMPRESSION RESULTS FOR 14- AND 36-DAY ESTANE-AGED PBX 9501.

Tensile and compressive σ_m and E values increase as a function of decreasing NP content, except for the tensile value of σ_m at a strain rate of $\sim 0.111 \text{ s}^{-1}$ and -15°C (not shown). This is similar to the behavior previously observed for PBX 9501 and VA PBX 9501 under the same conditions. This strain-rate inversion is observed for the two X-0557 lots at 23°C ; the reduction in NP has increased both the T_g values and the temperature at which this change in failure mechanism has occurred.

In tension, the ϵ_m values decrease with decreasing NP content; in compression, the ϵ_m values increase. In tensile studies of the pure binder (Estane/NP only), a decrease in NP wt% has also been observed to decrease ϵ_m , E , and σ_m values,¹¹ although the magnitudes of change are significantly larger in the pure binder than in the composite PBX 9501. These observations are consistent with the tensile properties of the composite being predominantly driven by the binder properties.

The X-0557 compositions (Table 1) show a $\sim 2 \text{ wt}\%$ increase in solid filler concentration as the NP wt% is lowered. The two X-0557 lots were pressed to a similar %TMD as the baseline PBX 9501. Tension and compression σ_m and E parameters correlate linearly with NP/Estane ratio, with HMX wt%, and with average specimen density (data not shown).

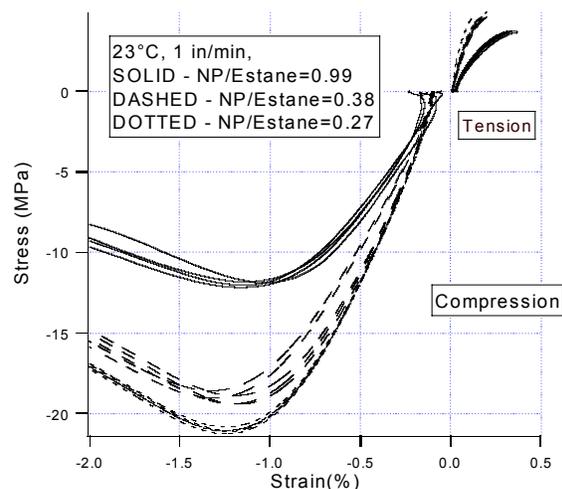


FIGURE 4: QUASI-STATIC STRESS-STRAIN CURVES (TOE-CORRECTED) FOR PBX 9501 AND TWO LOTS OF X-0557.

Again comparing the ratio of the tensile to the compressive modulus, the E_{50} ratio at -20°C goes from ~ 1.2 to ~ 1.34 as the NP content drops from 2.6 to 0.69 for both quasi-static strain rates. Similar to the VA PBX 9501 lots, the temperature dependence of the tensile properties appears to track the T_g shift of the binder.

SHPB stress-strain curves as a function of NP content at 22°C and 2000 s^{-1} are presented in Figure 5. At ambient temperature, a reduction in the NP content results in a near doubling of the peak stress.

The ambient temperature high-strain-rate strength data illustrated in Figure 6 exhibit a rapid transition between 0.9 and 2.5 wt% NP concentration that is not observed at either -15°C or 50°C, or in the low-strain-rate compression data. The variability in strength and sharpness associated with this transition will be further quantified by examining additional formulations between ~0.7 and 2.5 wt% NP.

Future aging studies should also

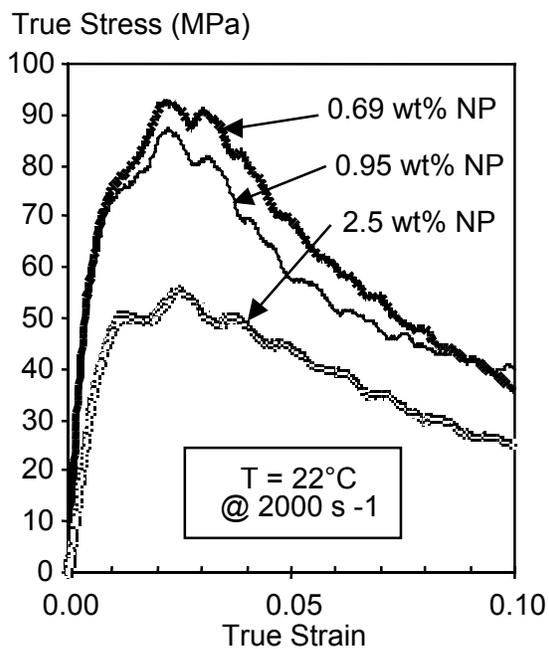


FIGURE 5: SHPB TESTS OF PBX 9501 AND TWO LOTS OF X-0557 AT 22°C.

explore the potential effects of NP gradients following NP migration from the surface. Studies involving more complex accelerated aging methods are currently underway. In addition, microscopic imaging techniques are being used to analyze PBX specimens for physical changes associated with aging.

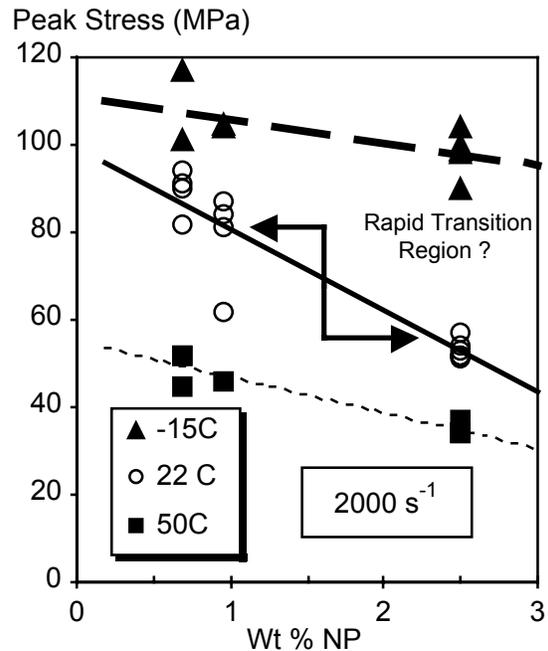


FIGURE 6: SUMMARY OF TESTS AT 3 TEMPERATURES, PBX 9501 AND THE TWO LOTS OF X-0557.

CONCLUSIONS

Two age-relevant topics have been explored for PBX 9501 using quasi-static (compression and tension) and dynamic (compression) mechanical properties testing. Large reductions of Estane M_w only modestly decrease the strength and stiffness properties of PBX 9501; however, large reductions in the NP content strongly increase the strength and stiffness properties. Quasi-static tension parameters measured for the different variations of PBX 9501 as a function of strain rate and temperature follow similar trends as the pure binder alone.

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