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D. M. Hoffman, K. T. Lorenz, B. Cunningham, F. Gagliardi

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Formulation and Mechanical Properties of LLM-105 PBXs[†]

D. Mark Hoffman, K. Thomas Lorenz, Bruce Cunningham and Franco Gagliardi

Lawrence Livermore National Laboratory

Livermore, CA

ABSTRACT

Eight different polymer binders were formulated with bimodal distributions of 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) in 5/95 weight ratio of polymer to explosive at the 25 gram level. The polymers evaluated included: Kel-F 800, Viton A, Oxy 461, Cytop A, Hyflon AD 60, Hytemp 5545, Technoflon PFR 91 and Technoflon P 459. LLM-105 had an average particle size of $35.6 \pm 0.6 \mu\text{m}$. This material was ground in a ball mill for 24 h to achieve a particle size of $0.72 \pm 0.02 \mu\text{m}$. Small angle light scattering measurements were used to obtain particle size distributions on both ground and unground LLM-105. Optical microscopy was used to characterize the morphology of the crystals. Bimodal mixes of approximately 75/25% coarse to fine LLM-105 were used in all formulations. Cylinders 1.27 cm diameter by 2.54 cm long were compression molded using 3 three-minute cycles at 105°C, except in the case of Cytop and Hyflon formulations which were molded at ~ 130°C. Densities varied between 94-98% of theoretical maximum. Stress strain measurements were made in compression at -30, ambient and 74°C at a strain rate of 0.0001 sec^{-1} . As expected, the mechanical strength scaled with temperature depending on the glass transition temperature of the polymer.

INTRODUCTION

The Energetic Materials Group at Lawrence Livermore National Laboratory continues to search for insensitive explosives (IHE) comparable to 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Recently LLM-105 has been shown to be slightly more sensitive than TATB, with improved initiation characteristics at low temperature[1, 2]. Unfortunately, preliminary crystallization produced high aspect ratio crystals. Formulation with needle-like crystals produced low density plastic bonded explosives (PBXs). Initial syntheses of LLM-105 also contained 8-10% ANPZ impurity. Recent re-oxidation of LLM-105 reduced the ANPZ content by about half and produced crystals

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with cube-like morphology averaging 35 μm on a side. The crystal density at ambient was 1.9097 ± 0.0005 g/cc. LLM-105 theoretical density was 1.919 g/cc. [3] Even at relatively high molding pressures (200 MPa \sim 30 ksi), PBXs formulations based on 2.5 and 5% Kel-F 800 or Viton A binders produced parts with low density (92-94% TMD). In this work we evaluated the effect of bimodal mixes of LLM-105 with 5% of a variety of binders on the density and compressive strength of the PBX.

Binders for insensitive explosives do not have to be shock absorbing elastomers so it should be possible to achieve more strength and structural integrity in PBXs designed with thermoplastics and IHEs, especially at elevated temperatures. Since the energy of the PBX varies as the square of the density, [4] polymers with densities of 1.85 g/cc or more were usually selected for more energetic PBXs. Thermoplastics with glass transitions (T_g) above the typical operating range but within the processing range ($80 < T_g < 130^\circ\text{C}$) of the explosive presses are of interest. Cytop A and Hyflon HD 60 are thermoplastics with densities of 2.03 and 1.93 g/cc and glass transitions of 104 and 110°C , respectively. The structures of the polymers investigated here are shown in Figure 1. As can be seen in the figure, all but one of these binders are fluoropolymers.

EXPERIMENTAL

Formulations were hand mixed, initially at the 1 gram level and after small scale safety testing was completed, scaled up to 25 grams. Twenty percent by weight binder in acetone solutions was used except for the perfluorinated polymers (Cytop A, Hyflon AD60, and PFR-91), which require special perfluorinated solvents. Approximately 75/25 LLM-105 coarse to fine solids ratio was used in all cases. Excess solvent was added as needed to obtain usable lacquer viscosity and/or a putty-like consistency of mix. PBXs were dried to constant weight in a forced air oven and ground into particles of about 5 mm or less by hand with mortar and pestle prior to compression molding. Each new PBX made from LLM-105 is designated as research explosive RX-55-XY. Table 1 lists the RX-55-series compositions described in this work. The theoretical maximum density (TMD) in the table was calculated assuming volume additivity.[5] Right circular

cylinders (1.27 cm diameter by 2.54 cm long) were compression molded at 105°C using three each three-minute dwells with 30 seconds of pressure release between dwells except for the thermoplastics. Average part densities are listed in Table 1 along with % TMD. To enable flow, thermoplastics must be pressed above their glass transition temperature. The Cytop A formulation was pressed at 120°C and the Hyflon AD60 at 130°C. Small scale safety data is given in Table 2. Extensive discussions of the small scale techniques are given elsewhere. [6-10]

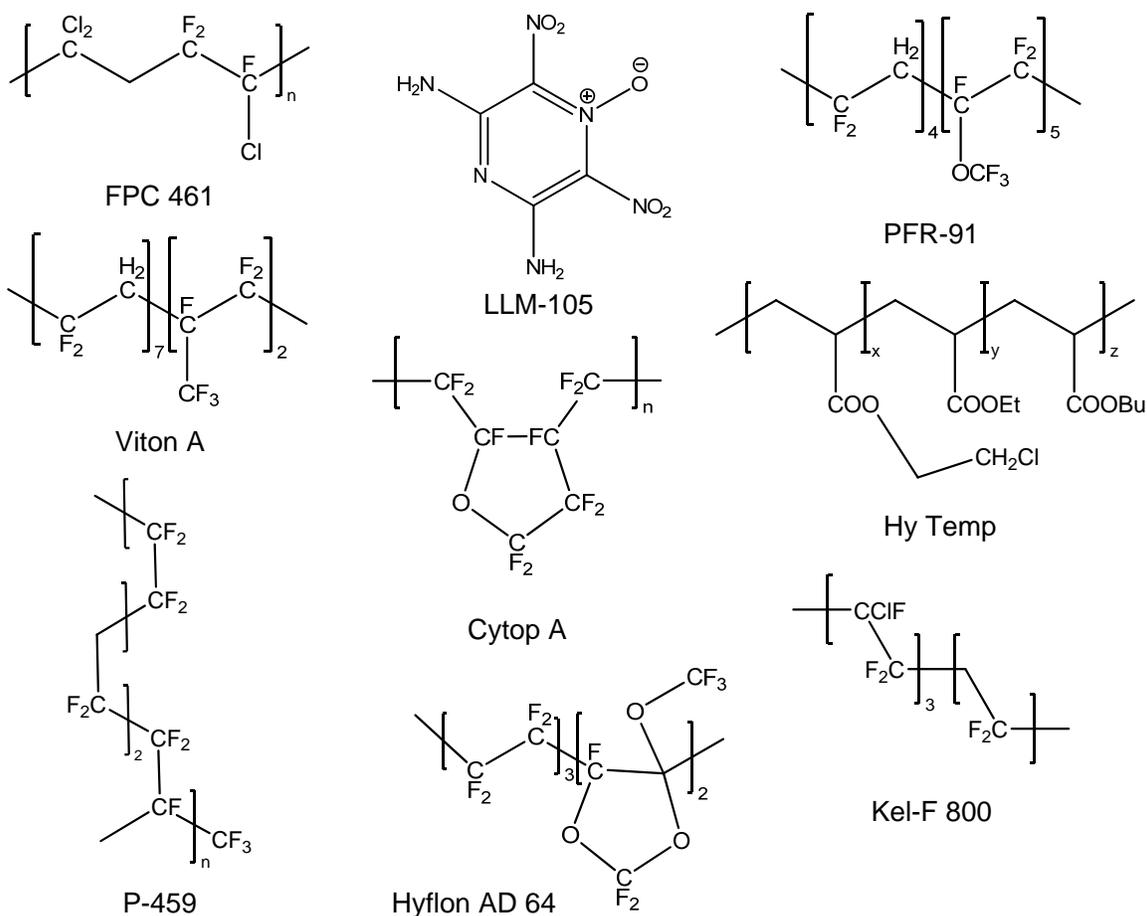


Figure 1. The structure of polymers evaluated as binders for LLM-105 (structure shown at top center) were all fluoropolymers except Hy Temp.

LLM-105 was ground as an aqueous suspension in a 0.38 liter ceramic jar mill using 1.3 cm ceramic cylinders for 24 h. This time was sufficient to remove most of the large crystals as can be seen in Figure 2. This figure also shows the change in the light scattering estimate of particle size distribution of LLM 105 as a function of grinding

time. As can be seen in the figure, the comminution process involves fracturing the edges of the crystal. In theory, one could grind until a 75/25 coarse to fine ratio was obtained or until most of the large crystals had been reduced to the size of the fractured particles. The latter approach was taken assuming it would be more reproducible.

Table 1. Compositions and densities of LLM-105 formulations used in this study.

	Solvent	binder	finer	coarse	TMD	ρ	%TMD
		(Wt%)	(Wt%)	(Wt%)	(g/cc)	(g/cc)	%
LLM-105	NA	0	0	100	1.9127*	1.9097	99.8
AA	Acetone	5.00	25.97	69.03	1.9044	1.814	95.0
AI	Acetone	4.97	25.98	69.05	1.9117	1.820	94.9
AK	Perfluoro	5.00	26.00	69.00	1.9117	1.686	87.9
AL	Acetone	5.02	25.88	69.11	1.9007	1.804	94.9
AM	Acetone	4.99	25.88	69.13	1.8090	1.777	98.2
AN	FC 43	8.65	25.05	66.30	1.9135	1.751	91.5
AO	Ethylacetate	5.00	26.00	69.00	1.9115	1.795	93.9
AP	Galdin HD	6.25	25.75	68.00	1.9174	1.835	95.8

*TMD of 95/5:LLM-105/ANPZ – approximate composition of reoxidized LLM-105

Table 2. Small scale safety data on RX-55-series formulations was very good.

RX-55-	5% Binder	DH50	Friction	DSC (Ton)	CRT (120)
LLM-105		104 cm	36		
AA	Viton A	>177.4 cm	36 Kg	317°C	0.07 cc/g
AI	Kel-F 800	>177.4 cm	36 Kg	321.4°C	0.14 cc/g
AK (A)	Cytop A	>177.4 cm	36 Kg	324.4°C	0.04 cc/g
AL	Oxy 461	133 cm	36 Kg	322.9°C	0.10 cc/g
AM	Hy-Temp	>177.4 cm	36 Kg	307.9°C	0.09 cc/g
AN	Hyflon AD60				
AO	Tecno P 459	99 cm	36 Kg	313.5°C	0.03 cc/g
AP	Tcno PFR91	138 cm	36 Kg	317.4°C	

Mechanical properties were measured on right circular cylinders 1.27 cm in diameter by 2.54 cm long weighing approximately 6 grams in compression at strain rate of 0.0001 s^{-1} using hydraulic MTS equipment. A description of the method and equipment is given elsewhere. [11]

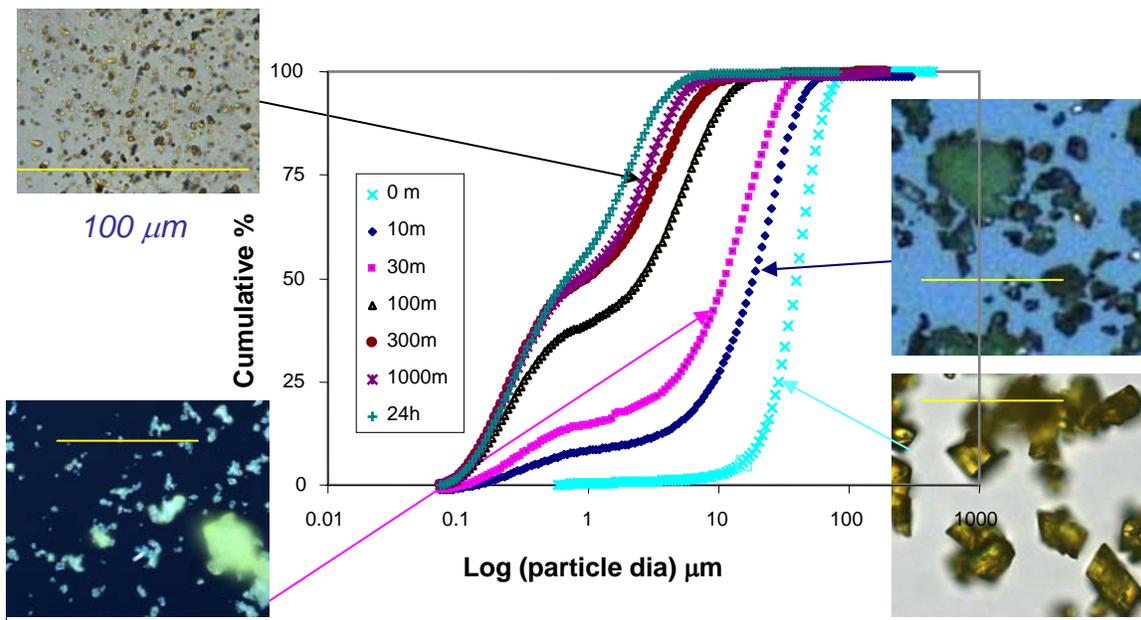


Figure 2. Optical micrographs and light scattering showed that the particle size distribution was reduced from $\sim 35 \mu\text{m}$ to $0.3\text{-}0.5 \mu\text{m}$ in 24-h in the jar mill. The bar in all micrographs is $100 \mu\text{m}$ and arrows associate a micrograph with its scattering curve.

RESULTS & DISCUSSION

Thermal stability of LLM-105 was superior to conventional high explosives. The decomposition of small quantities begins above 300°C . Differential Scanning Calorimetry (DSC) of these formulations in Figure 3 showed similar decomposition characteristics for all fluoropolymer binders, but a 7-14 degree reduction in onset temperature for RX-55-AM where the binder was an acrylic copolymer. Of the fluoropolymers, Hyflon AD 60, Viton A, Technoflon P 459 and Kel-F 800 do not begin to exotherm until 375°C and Cytop A shows no exotherm until about 450°C . Extensive thermal studies have been done on RX-55-AA [10] and these results are similar.

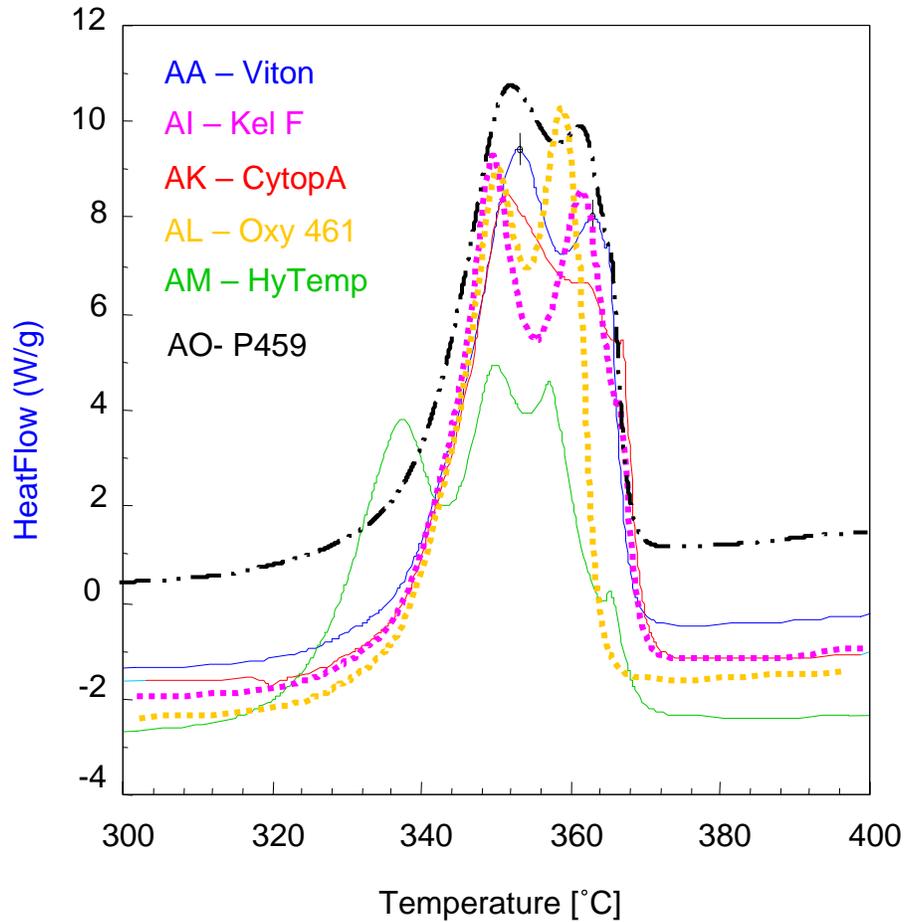


Figure 2. DSC traces of RX-55-series explosives are all similar except for the acrylic binder in RX-55-AM which decomposed almost 10°C lower than the others.

Table 3. Temperature (T) dependence of Young's Modulus, $E_y(T)$, and ultimate strength, $\sigma(T)$, of the PBX depended dramatically on the binder.

RX	Binder	$\sigma(-30)$	$E_y(-30)$	$\sigma(23)$	$E_y(23)$	$\sigma(74)$	$E_y(74)$
#/units		(MPa)	(GPa)	(MPa)	(GPa)	(MPa)	(GPa)
AA	Viton A	80.6	8.96	15.6	0.921	7.4	0.263
AI	KF 800	84.4	8.35	47.1	5.48	11.5	0.513
AK	Cytop A	83.3	7.26	30.2	1.35	23.5	1.07
AL	Oxy 461	81.2	7.04	63.9	6.62	12.4	0.798
AM	HyTemp	91.4	3.01	12.9	0.182	5.7	0.096
AN	Hyflon	41.0	0.89	34.3	2.37	29.4	1.96
AO	P 459	-	-	12.0	0.86	6.7	0.44
AP	PFR 91						

To a first approximation, the binder in these PBXs acts as the continuous phase, so the mechanical properties will depend strongly on the mechanical properties of the binder.[4] Cooling below the glass transition (T_g) of the binder changes its modulus from MPas to GPa or about 3 orders of magnitude. Figure 3 shows this effect for Viton and Kel-F 800 formulations. At -30°C , below T_g for both binders, the compressive moduli (8.96 and 8.36 GPa) and strengths (80.6 and 84.4 MPa) of the PBXs are similar. Strength is the maximum in the stress-strain curve, often called ultimate strength. The T_g of Kel-F 800 is close to ambient while Viton's T_g is -18°C , thus the compressive modulus and strength of RX-55-AI (5.48 GPa and 47.1 MPa) are significantly higher than RX-55-AA (0.92 GPa and 15.6 MPa) under ambient conditions. When the glass transition of both polymers has been exceeded (74°C), the moduli (0.26 and 0.51 GPa) and strengths (7.4 and 11 MPa) of the composite PBXs are reduced but become similar. Although there is a

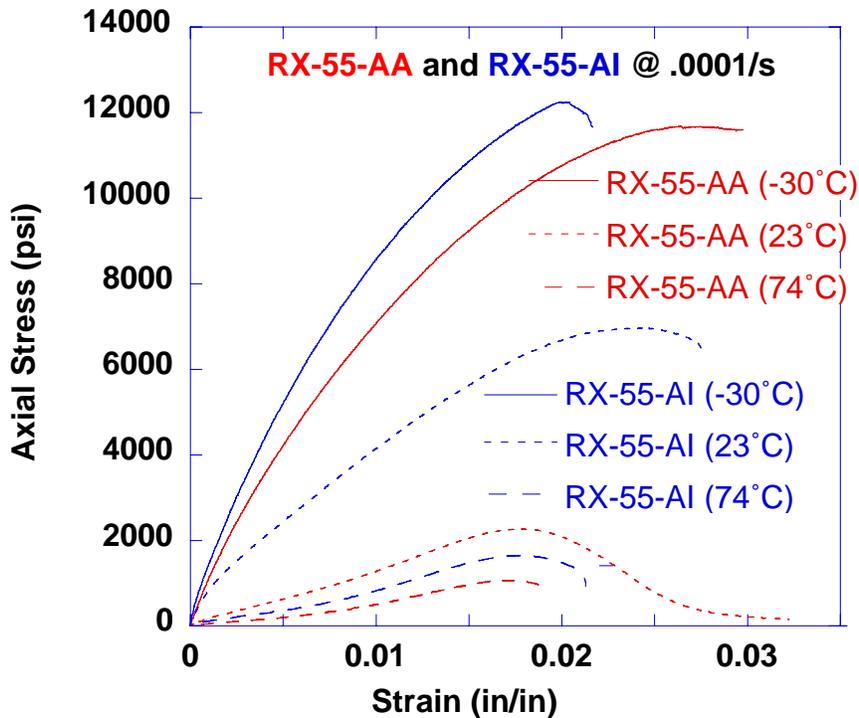


Figure 3. Compressive stress-strain curves at 3 different temperatures for Viton (AA) and Kel-F (AI) based RX-55-series explosives show the effect of the higher glass transition temperature of Kel-F 800 as an improvement in modulus and strength compared to Viton at ambient.

3 order of magnitude change in binder modulus, fortunately, the PBX modulus changes only by about an order of magnitude when the binder glass transition is exceeded. If a

binder with T_g greater or less than the operational temperature is used then the modulus and strength are expected to remain high or low, respectively, throughout the use environment. Figure 4 shows the stress-strain curves of RX-55-AN. The Hyflon binder T_g is approximately 110°C so the strength and modulus change only slightly between $-30 < T < 74^\circ\text{C}$. Table 3 lists Young's modulus and ultimate strengths of the different formulations. A binder with a high degree of crystallinity is probably not good because there is less polymer chain to interact with the explosive surface. Small amounts of crystallinity in the binder, however, can have a positive affect on the PBX mechanical properties by increasing the modulus above T_g . [12] If the binder were able to stress crystallize during deformation, some self reinforcing could occur which might be effective at increasing elongation in the PBX. Young's modulus and ultimate stress of these formulations is given in Table 3.

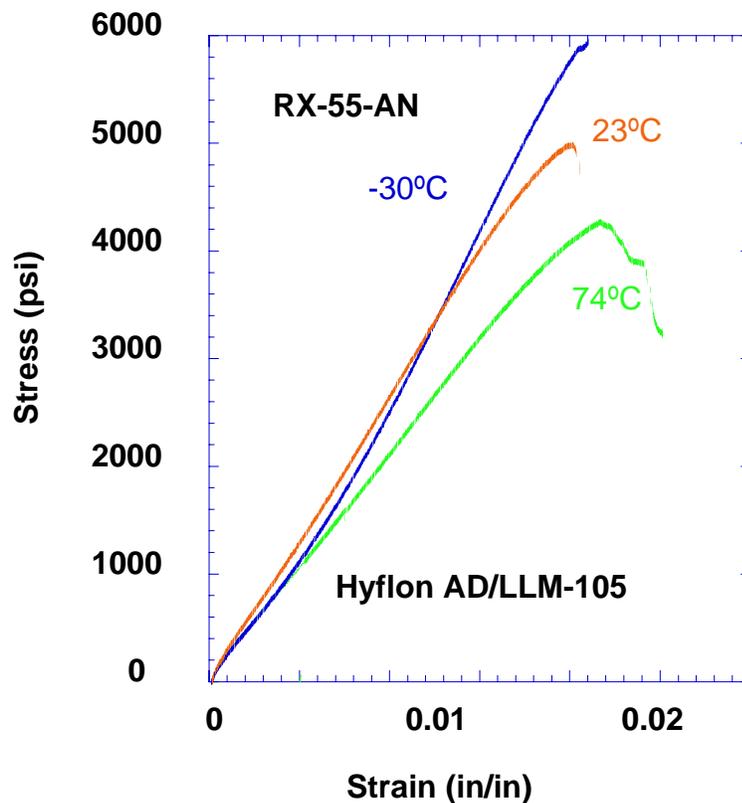


Figure 4. Using a binder with T_g above the measurement temperature results in moduli which are almost independent of temperature, although the strength in this instance is less than Kel-F or Viton PBX strengths below T_g .

Strain to failure and ultimate elongation can be increased if the volume fraction of the binder is increased. This occurs at constant weight fraction if the density of a binder is low compared to LLM-105. Thus one would expect the acrylic copolymer HyTemp to have better elongation characteristics than the more dense fluoroelastomers (Viton A, Technoflon P459 or Technoflon PFR 91). This is clearly seen in Figure 5 where stress-strain curves of RX-55-AO (Technoflon dotted lines) and RX-55-AM (HyTemp dashed lines) above T_g are compared. Interestingly, the 74°C strains to failure were less than those measured at 23°C, which is consistent with rubber elasticity theory. Differences in ultimate strength seem to be associated with slight differences in density, but more work needs to be done to confirm this.

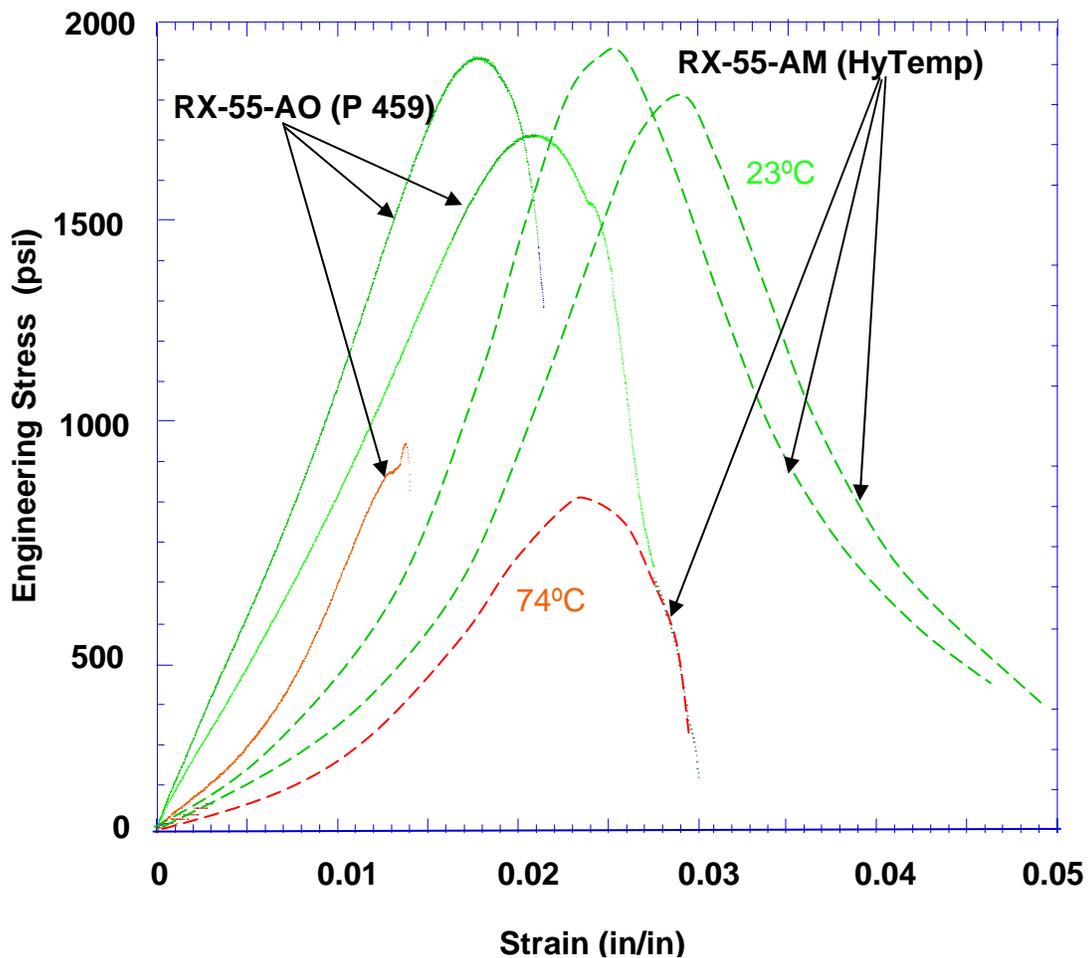


Figure 5. Above T_g , higher volume fraction of binder (RX-55-AM) results in higher elongation even though weight fractions are 95/5: LLM-105/binder in both cases.

Some results which do not fit conventional ideas about mechanical properties of PBXs include the very early nonlinearity of the stress-strain curves, the disparity in strengths of the different PBXs below T_g , and the apparent stress hardening of high T_g binders as a function of elongation. The most linear behavior at low strain is at the lowest temperature. The Viton, Cytop and Oxy formulations have nearly identical traces at -30°C and shortly beyond 0.02% show only slight curvature. The apparent stress hardening, as shown in Figure 5, for PBXs at temperatures above their binder T_g is associated with rubber elasticity, but that seen in Figure 4 for Hyflon and Figure 6 for Oxy 461 at temperatures below T_g is not understood.

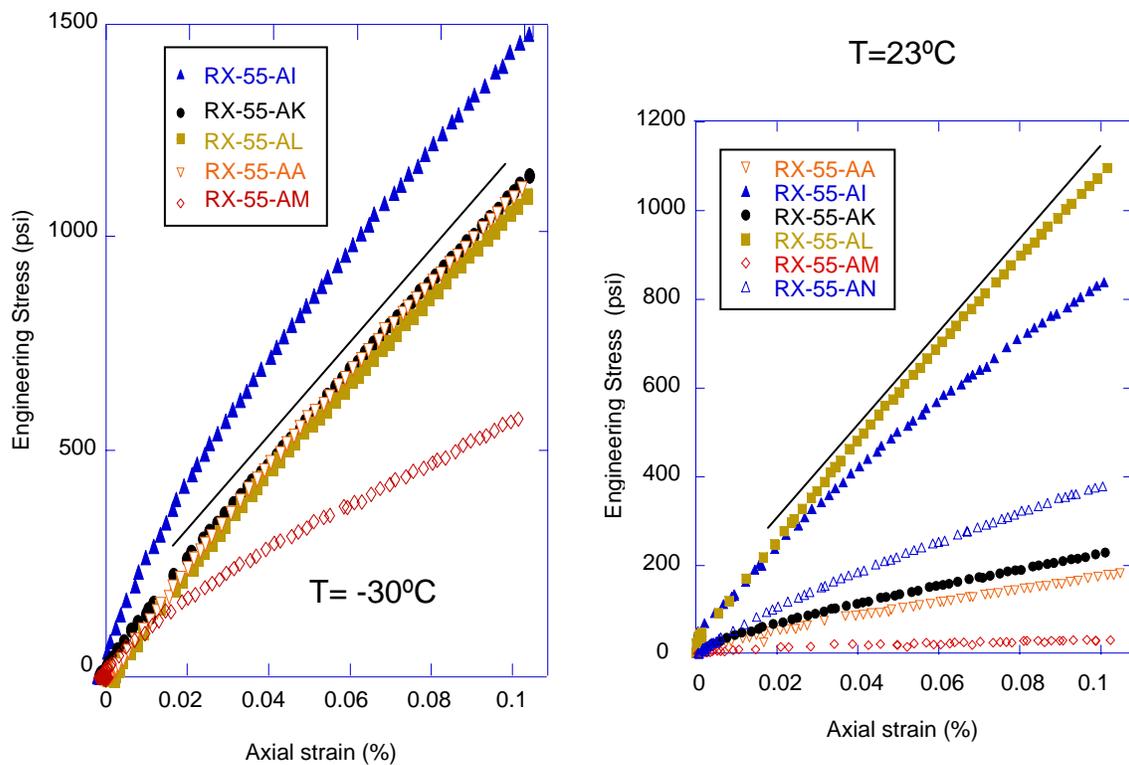


Figure 6. Early stress strain behavior, from which modulus data were calculated are often not linear.

CONCLUSIONS

When designing LLM-105 formulations for mechanical properties, high T_g binders produce PBXs with nearly constant modulus and strength at temperatures below T_g . In order to process these formulations, the binder T_g must not be higher than equipment temperature capability. Bimodal formulations can increase strength and density. Increasing the volume fraction of the binder tended to improve strain to failure, but the

energy of the PBX will be reduced because either TMD will be reduced or the amount of inert will increase. Strength and modulus of the PBX depend to some extent on the pressing density. Since only small quantities of PBXs were produced, the effect of density could not be examined thoroughly. Orientation effects, such as those found in TATB, have not been evaluated. Anomalous stress hardening of the higher T_g PBXs tested below the binder glass transition is currently not understood.

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