

"Dynamic Mechanical Signatures of Aged LX-17-1 Plastic Bonded Explosive"

D.Mark Hoffman
hoffman2@llnl.gov
Lawrence Livermore National Laboratory
Livermore, CA 94550

Introduction

The insensitive explosive LX-17-1 is used as the main charge in modern nuclear weapons. This plastic bonded explosive is a composite of 92.5% wet-aminated, 1-3-5-triamino-2-4-6-trinitrobenzene (TATB) and 7.5% inert binder KF-800. KF-800 is a copolymer of chlorotrifluoroethylene and vinylidene fluoride in approximately 3:1 mole ratio manufactured by 3M Corporation. This copolymer will crystallize when annealed above its glass transition temperature.¹⁻⁵ TATB is an explosive whose crystals have a graphitic structure.⁶

Although the static mechanical properties of LX-17 are known^{7,8} these results were only measured at a few temperatures and rates. Limited dynamic mechanical data on other explosives has been published^{9,10}, but no systematic study of LX-17-1 has been done. This report is an attempt to generate baseline and stockpile aged dynamic mechanical properties of LX-17-1.

Experimental

Specimens of LX-17 were machined from historical samples, core tests, or components from actual weapons in stockpile stored under a variety of conditions described in Table 1.

Results and Discussion

The KF-800^{1, 11, 12} binder in LX-17 has three relaxations in its dynamic mechanical spectrum which are expected to be observed in the PBX also. A low temperature β -relaxation occurs at approximately -40°C at 1 Hz. The glass transition occurs between 30 and 35°C at 1 Hz. As the binder crystallizes, its modulus between the glass transition and the melting temperature increases by more than an order of magnitude.

The magnitude of the peak in the loss modulus and tangent delta associated with the glass transition decreases with increasing crystallinity of the binder. When crystals form in a polymer, there will sometimes be a relaxation peak just prior to the melting temperature.¹³ This peak will vary with crystallite

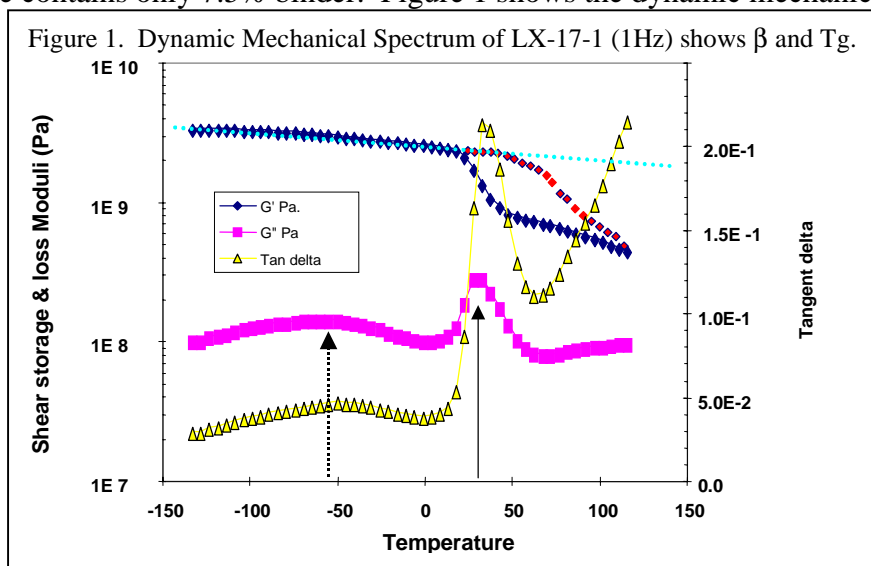
Table 1. Sample histories of LX-17-1 used in these experiments.

Sample ID	TATB [↓]	History/Remarks
LX-17A	A-005	Amorphous binder, LX-17-1
LX-17B	A-005	Thermal cycled 8 yr., PTX thermal cycle*
LX-17C	A-002	Taken from stockpile after 7.08 years
LX-17D	A-005	Stored 8.1 yr. at ambient in core test.
LX-17E	A-002	Taken from stockpile after 9.92 years
H2	A-002	Historical billet of lot 002 stored in bunker
H5	A-005	Historical billet or lot 005 stored in bunker
T-02 SRR	H-007	Ground test unit - shake rattle & roll test
T-04 SRR	H-007	Ground test unit - shake rattle & roll test

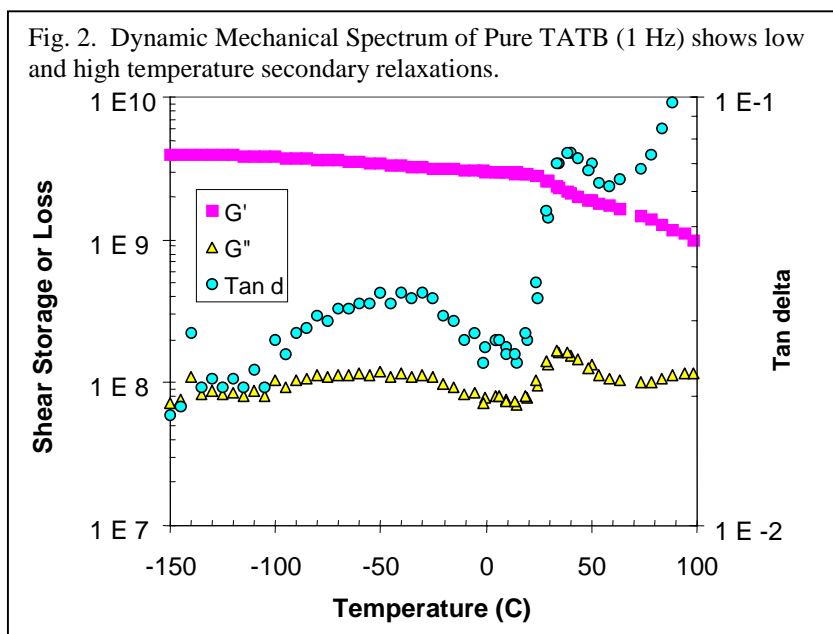
*Work performed under the auspices of the US Department of Energy by LLNL under Contract W-74050Eng-48.

perfection and crystallization temperature. In KF-800 it has been observed³ at about 80°C in samples crystallized for several weeks at 50°C.

The binder transitions in the dynamic mechanical spectrum of LX-17-1 were less dramatic since the explosive contains only 7.5% binder. Figure 1 shows the dynamic mechanical spectrum of LX-17-1 plastic bonded explosive where crystallinity has been removed by melting the binder prior to making the measurement. A very broad β -relaxation was observed as a peak in the loss modulus at about fifteen degrees below the relaxation maximum in the polymer, -55°C at 1-Hz (indicated by a dotted arrow in the figure). The breadth of this relaxation makes estimating the exact maximum difficult. As the temperature is increased, the binder passed through its glass transition, resulting in a peak in the loss modulus at about 30°C at 1 Hz (solid arrow).



The insensitive explosive TATB can be pressed into parts and machined without any binder, but this produces poor ultimate properties. Dynamic mechanical measurements made on pure TATB showed two relaxations over the temperature range from -150 to 120°C. As can be seen in Figure 2, the low temperature relaxation occurred at -45°C at 1 Hz. The mechanism responsible for this relaxation is not known, but may be associated with the onset of motion of the hydrogen bonded amine-nitro groups on TATB. The high temperature relaxation occurred at 34°C at 1 Hz. This relaxation seems to be associated with irreversible growth of TATB and the discontinuity of the c-axis expansion coefficient⁶ near this temperature.



1. The β -relaxation: As the temperature was increased from -150°C to 0°C , a weak, very broad, anelastic relaxation generally associated with the onset of molecular motion in the binder or explosive¹⁴ was observed as a peak in the loss modulus and tangent delta at -65 and -55°C , respectively. In LX-17-1 the maximum in this relaxation occurred at about 15 to 25°C lower temperature than in the pure binder.³ The shear loss modulus peaks from historical pressings, stockpile and core test specimens, and an amorphous sample of LX-17-1 are shown in Figure 3. All data shown in the figure was collected at 1 Hz. The temperature dependence of frequency, $\omega(T)$, in the β -relaxation usually follows an Arrhenius relationship:

$$\omega(T) = Ae^{-[E/RT(\text{peak})]} \quad (1)$$

The apparent activation energy of the G'' relaxation was 125 ± 20 KJ/mole (25 ± 5 Kcal/mole). The apparent activation energy for the tan delta relaxation was 75 KJ/mole (18 ± 5 Kcal/mole).

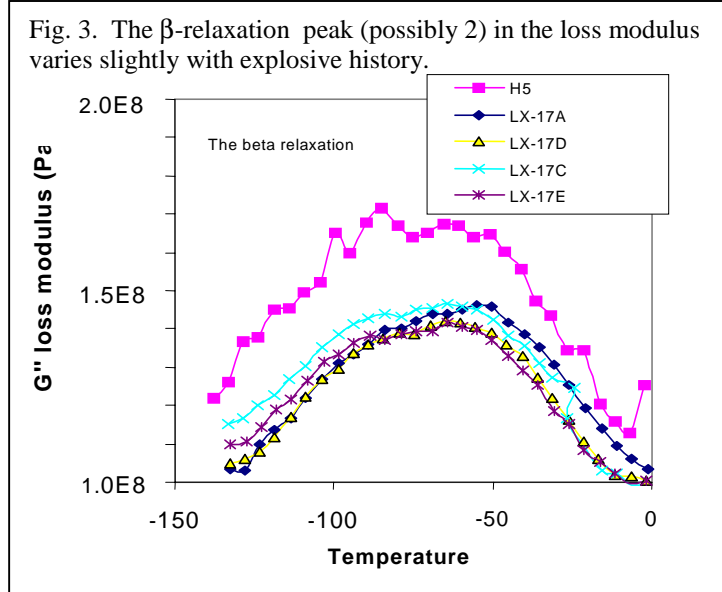
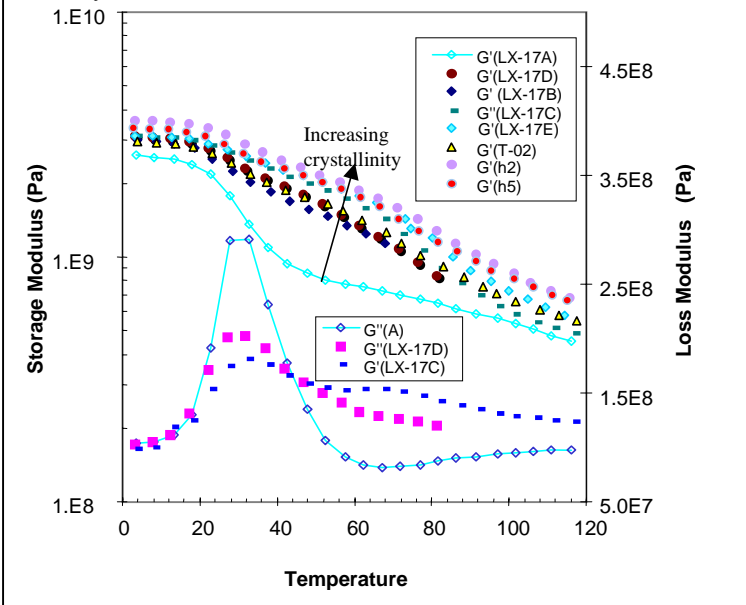


Fig. 3. The β -relaxation peak (possibly 2) in the loss modulus varies slightly with explosive history.

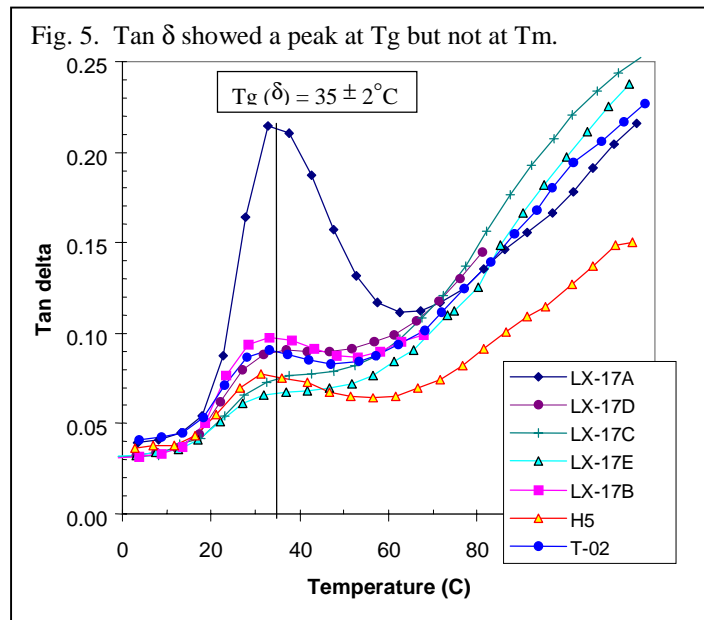
2. The Binder Glass Transition: The glass transition temperature of KF-800 occurs over about 40 degrees, from 10 to 50°C . The reduction in shear storage modulus (G') of LX-17-1 from about 3 to 0.7 GPa over this temperature range reflects this binder transition from a glassy solid to a rubbery elastomer. Figure 4 shows the shear storage modulus as a function of temperature for most of the LX-17-1 specimens tested. All of the results are for first runs except G' (LX-17A) which is a second run of G' (LX-17D). The first runs all show higher modulus above the glass transition than the second run because of crystallinity in KF-800.

The peaks in the shear loss modulus (G'') and tan delta (δ) were consistent with the glass transition temperature of the binder³. In all of the LX-17-1 samples tested, this peak occurred at $30 \pm 2^{\circ}\text{C}$ and $35 \pm 2^{\circ}\text{C}$, respectively, at 1 Hz. In Figure 5 the tan δ at 1 Hz for various LX-17-1 samples corresponding to the storage modulus data in Figure 4 showed no evidence of plasticization (T_g shifted downward in temperature compared to pure binder) or anti-plasticization

Fig 4. Shear storage modulus of LX-17 increased with crystallinity of the binder.



(T_g increasing with filler). The glass transition at 1 Hz in KF-800 lot 629³ was between 30-32°C. The intensity of the peak varies inversely with binder crystallinity but the exact degree of crystallinity in the binder has not been determined for these samples. The amorphous sample (LX-17-1A) gave the most intense peak while the stockpile returns gave the least. The G'' baseline below T_g , which should be independent of crystallinity, is approximately the same for all samples except H5 and the SRR sample. While the baseline above T_g is lowest for the amorphous sample and highest for the stockpile returns. The baseline of tan delta is fairly uniform except for the historical sample H5. Since tan delta is G''/G' , the behavior of loss and storage moduli follow each other in all samples except H5. The magnitude of the loss modulus above the transition follows the relationship: $G''\{\text{Thermal cycled (B)}\} \cong G''(\text{historical}) < G''(\text{SRR}) \cong G''(\text{ambient}) < G''(9 \text{ and } 10 \text{ yr. stockpile})$. This is consistent with a varying degree of crystallinity in these samples.



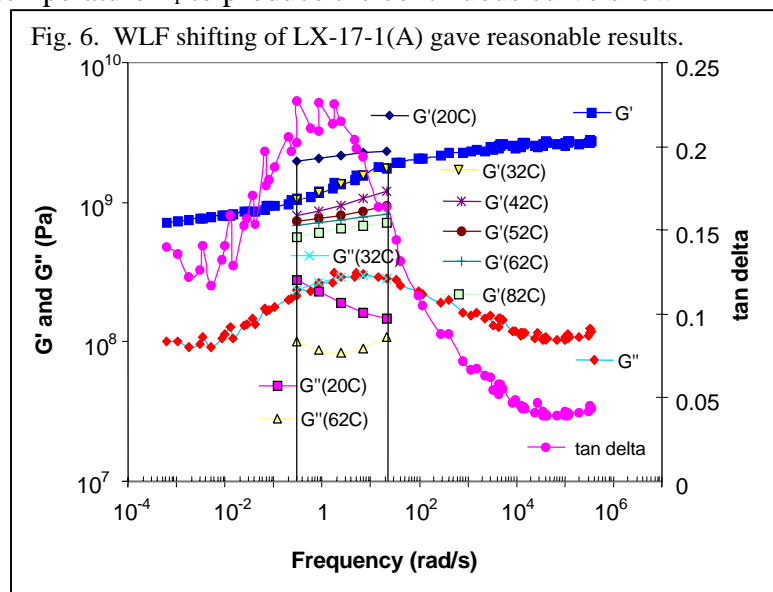
2. Time-Temperature Superposition:

When long time or low frequency behavior is inconvenient to measure, in some instances modulus measurements can be made over short frequency spans at incremental temperatures and shifted about a reference temperature to cover a much larger time or frequency range¹⁵. For a wide variety of amorphous polymers, the amount of shift has been shown to follow the WLF relationship:

$$\log a(T) = [C_1(T - T_r)]/[C_2 + T - T_r] \quad (2)$$

where $a(T)$ is the amount a modulus measurement made at frequency ω and temperature T must be shifted with respect to the reference temperature T_r to produce the continuous curve shown in Figure 6. C_1 and C_2 are constants.

When the data for LX-17-1A were shifted about T_r of 32.5°C, C_1 and C_2 were calculated to be 21.1 and 131.2, respectively. Shear storage moduli at constant temperature and at 5 frequencies from 0.628 to 62.8 rad/s are shown between the two lines in the center of the figure. The data were shifted to generate the G' versus ω curve from 10^{-4} to 10^7 rad/s about a reference temperature of 32°C. Shear loss moduli and tan delta curves were also shifted as a function of frequency and shown in the figure. The data showed an increase in stiffness with



frequency. In Figure 7 a computerized shift factor generated by minimizing residuals from G' data from -20 to 80°C is compared to the WLF fit (solid line). The WLF relationship fits well above 0°C , but shifts too much below this temperature.

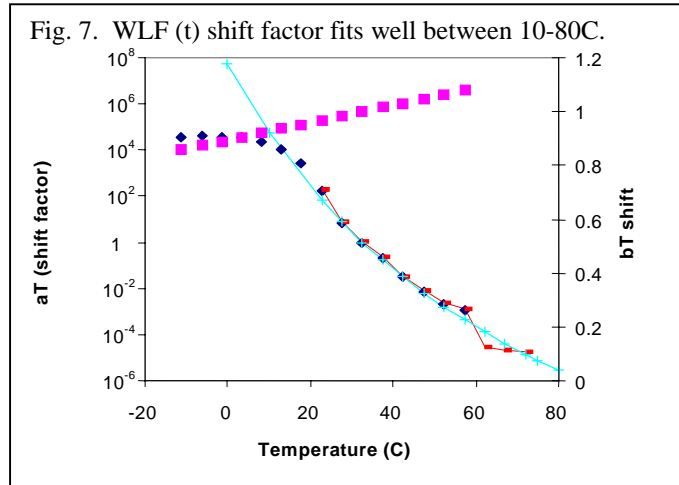
When attempts were made to fit WLF or optimized shift factors to data from one dynamic mechanical function of LX-17-1 samples with crystallinity, the other dynamic mechanical functions could not be shifted in a continuous manner. Once the binder begins to crystallize, the time-temperature superposition principle can no longer be applied. Flowers also found this result for pure binder in reference 11.

3. Effect of Crystallinity: Above the glass transition the crystallinity of KF-800 increases slowly with time^{1-4,8}. Any thermal excursion above about 30°C produces sufficient mobility in the binder for crystallites to grow. Crystallization below T_g may occur over very long times but has not been studied. Because of the comonomer incorporated in the KF-800 chain, crystallinity is low^{6,7}, typically less than 10-20 percent and develops over long times. The perfection of these crystallites depends on crystallization temperature and incorporation of comonomer.

The insert in Figure 1 (diamonds) shows the shear storage modulus of crystalline LX-17-1E taken from stockpile after 9 years in service compared to that of LX-17-1A with amorphous binder. Above the glass transition temperature the shear storage modulus is significantly higher in the stockpile sample than in the sample with amorphous binder. Crystallinity effects for various LX-17-1 samples are shown in Figure 4. Amorphous KF-800 in LX-17-1A should serve as a baseline for comparison. Polymer crystals generally increase in perfection as their growth temperature approaches their melting temperature. The actual melting point of the crystal reflects this improved crystallite perfection. Crystallization of copolymers is complicated by the exclusion of non-crystalline monomer in the backbone chain. Although more perfect crystals form at higher crystallization temperatures, some parts of the chain can no longer be incorporated in the crystal structure. This causes the melting temperature to increase but the crystallinity to decrease.

Conclusions

Three relaxations were found in the dynamic mechanical properties of LX-17-1. The β -relaxation occurred at a lower temperature (-65°C) in LX-17-1 than in either the binder or pure TATB. Its maximum was influenced by the crystallinity of KF-800. The glass transition of KF-800 is observed at the same temperature (30 - 32°C) in LX-17-1. The change in modulus in the PBX as it passed through T_g was substantially less than that observed in the binder. When the binder is amorphous, a WLF relationship can be used to shift temperature and frequency over approximately 10 orders of magnitude. The storage modulus above T_g increased by up to 3.2 times as binder crystallinity increased. The time-temperature superposition principle could not be applied once the binder has crystallized.



Linear thermal expansion was measured during the dynamic mechanical measurements. Values were consistent with other measurements, but often higher. Anomalous expansion was observed in LX-17-1 with crystalline binder. The linear coefficient of expansion was larger by almost a factor of 3 when the binder was crystalline compared to amorphous binder in LX-17-1.

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