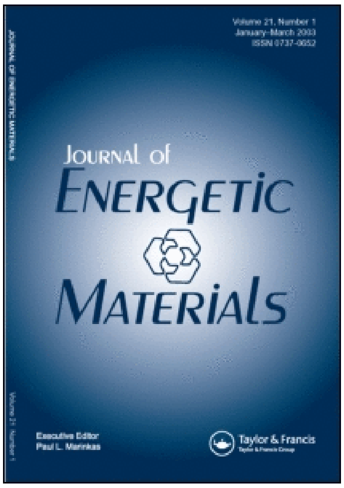

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Dynamic mechanical signatures of aged LX-17-1 plastic bonded explosive

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DYNAMIC MECHANICAL SIGNATURES OF AGED LX-17-1 PLASTIC BONDED EXPLOSIVE*

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ABSTRACT

The complex shear modulus of the plastic bonded explosive (PBX) LX-17-1 from stockpile returns, core tests and historical billets was measured over the temperature range from -150 to 120°C at five frequencies from 0.1 to 10 Hz. LX-17-1 is composed of **92.5% insensitive high explosive triaminotrinitro-benzene (TATB)** and 7.5% plastic binder, KF-800. Three relaxations were observed as peaks in the loss modulus and tangent delta in various samples of LX-17-1. The low temperature β-relaxation, a very broad relaxation, occurred between -50 and -65°C depending on sample history. The glass transition of the binder was observed as a peak in the loss modulus at 30 ± 2°C at 1 Hz. No evidence of

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plasticization or anti-plasticization caused by the explosive filler or binder crystallization was observed. When LX-17-1 was stored above its glass transition, the binder crystallized and occasionally the α-relaxation, associated with melting of the crystal, could be resolved as a peak in the loss tangent at approximately 80°C. More often only a change in slope or broadening in the loss peak was observed. The shear storage modulus increased depending on binder crystallinity by a factor of up to 3.2 at temperatures between the glass transition and melting point of the binder. Crystallization is slow so the dynamic moduli of LX-17-1 with amorphous binder could be measured before recrystallization occurred. The weak relaxation of the pure TATB at about 34°C was hidden by the glass transition of the polymer binder. Secondary crystallization of the binder may be responsible for the PBX stiffening over time as indicated by a very slight increase in storage modulus of aged LX-17-1 from stockpile and accelerated aging tests. Some increase in modulus was also found below T_g in aged samples that may indicate other mechanisms were responsible for the observed increase in stiffness.

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]. LX-17 is prepared by coating a water slurry of TATB with a solution of KF-800. When the solvent is removed, the resulting "molding powder" consists of spherical aggregates of TATB coated with polymer. This "molding powder" is dried, isostatically pressed into billets at 105°C at 140 MPa (20 Ksi), cooled to ambient and machined into device parts.

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

LX-17-1 Insensitive High Explosive Samples

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

Dynamic Mechanical Measurements

Complex shear moduli were measured on a Rheometrics Mechanical Spectrometer (RMS) model 800. Rectangular specimens 6.35 cm (2.5") long by 1.27 cm (0.5") wide by 0.3175 cm (0.125") thick were machined to approximately 0.03 cm tolerances. The RMS 800 has special fixturing to hold these samples inside a thermal chamber cooled by gas generated from liquid nitrogen and heated by an electronic heating element. Five frequencies were measured at a given temperature. Temperature was controlled to approximately ±0.3°C during the frequency sampling. Temperature was incremented approximately 5°C and allowed to equilibrate for one minute prior to resumption of modulus measurements. Slight tensile load is applied to the sample to compensate for thermal expansion and prevent buckling. The maximum percent strain was set to 0.5%. Frequency was varied from 0.1 to 10 Hz in 5

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 heated to 120°C, then cooled to ambient and tested
LX-17B	A-005	Thermal cycled 8 yr., standard PTX thermal cycle* core test
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	Taken from historical billet of lot 851-002 stored in bunker
H5	A-005	Taken from historical billet or lot 851-005 stored in bunker
T-02 SRR	H-007	Taken from ground test unit - shake rattle & roll test
T-04 SRR	H-007	Taken from ground test unit - shake rattle & roll test

* Standard PTX Thermal Cycle - heat to 71°C and hold for 28-d, cool, cycle 4 times from -54 >T>71°C and hold for 24-h, cycle 8 times from 65> T> 35°C, cool to ambient.

↓ TATB manufactured by A=Aerojet or H=Hercules, -00X indicates last 3 digits of Holston lot number associated with the LX-17-1 lot.

logarithmic increments during each temperature interval. Figure 1 shows a sketch of the fixturing. All explosives testing was

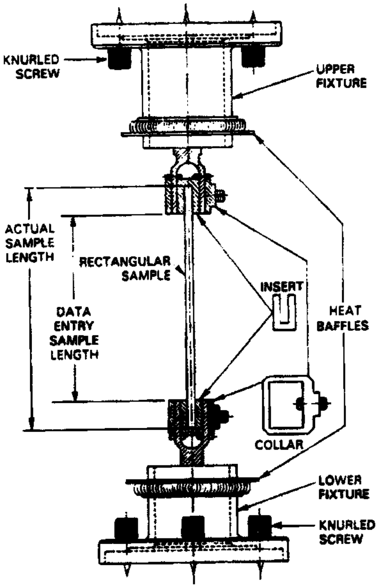

FIGURE 1. Rectangular sample and fixturing setup for testing of LX-17-1.

performed remotely in a ¼" steel cell. For the rectangular torsional specimen geometry, a sinusoidal strain, γ^* is imposed on the specimen according to the relationship:

$$\gamma^* = \gamma_0 \exp\,[i(\omega t)] \qquad (1)$$

where γ_0 is the maximum strain amplitude, ω is the oscillating frequency and t is the time. The shear stress τ^* is measured as a torque which lags behind the imposed strain by some time δ/ω according to the relationship:

$$\tau^* = \tau_o \exp [i(\omega t + \delta)] \quad (2)$$

where δ is the phase angle of this lag. In the linear viscoelastic regime, the modulus is independent of strain so the complex shear modulus is given by:

$$G^* = (\tau^*/\gamma^*) = (\tau_o/\gamma_o) e^{i(\delta)} = G' + iG" \quad (3)$$

Where G' is the shear storage modulus (real component of G*) and G" is the shear loss modulus (imaginary component of G*). The strain, γ, on a sample of thickness T, width W, and length L is essentially a geometric constant, $K(\gamma)$, times the angular displacement θ in radians:

$$\gamma = T\theta[1 - 0.378(T/W)^2]/W = K(\gamma)\theta \quad (4)$$

The stress can be calculated from a geometric constant $K(\tau)$, the transducer torque M and the gravitational constant g_c (98.07 Pa/g):

$$\tau = Mg_c\{[3 + 1.8(T/W)]/WT^2\} = K(\tau)M \quad (5)$$

The ratio of G''/G' is the tangent of the loss angle delta. When a relaxation occurs in a material, there is a time or frequency dependent effect on the modulus. This results in a reduction of the storage modulus and a maximum in the loss modulus and tangent delta. Various types of transitions show such relaxations including glass transitions, secondary relaxations and crystallization or melting phenomena.

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 or 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 perfection and crystallization temperature. In KF-800 it has been observed[3] 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 2 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

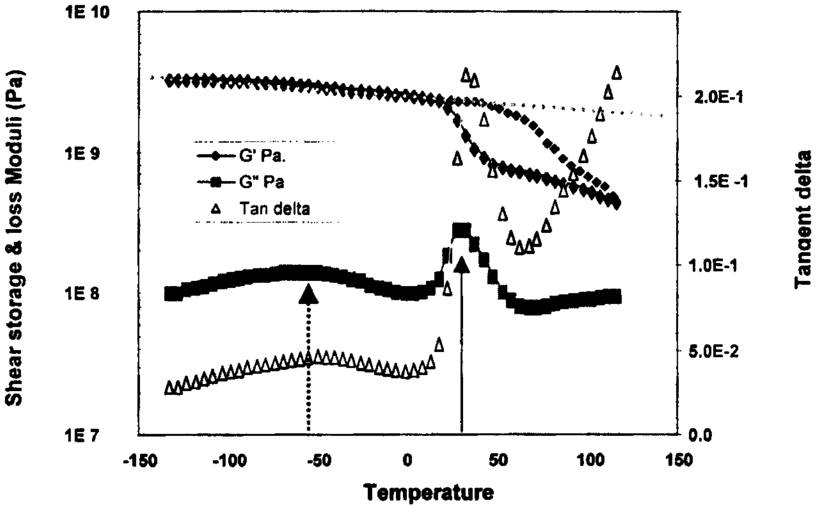

FIGURE 2. Dynamic mechanical measurements of LX-17-1 at 1 Hz show 2 peaks in the loss modulus and tangent delta associated with the binder glass transition (30°C) and a low temperature β-relaxation (-55°C) indicated by solid and dotted arrows, respectively.

figure). The breadth of this relaxation makes estimating the exact maximum difficult. More than one relaxation could be concealed here, but no conclusive evidence of multiple peaks was found in the frequency sweeps from 0.1 to 10 Hz. 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 in Figure 2 (solid arrow). The glass transition in KF-800 occurs over a temperature range of about 30°C during which the shear storage modulus of LX-17 is reduced from 2.6 GPa at 0°C to 0.81 GPa at 50°C, a factor of 3.2, when no crystalline reinforcement is present in the binder. This change in stiffness is much more pronounced in the pure binder going from 0.48 GPa to 0.001 GPa for amorphous KF-800 (more than three orders of magnitude). The TATB acts as reinforcing filler for the binder in its rubber plateau region. As little as 7.5% binder has a dramatic effect on the mechanical properties of this highly filled explosive.

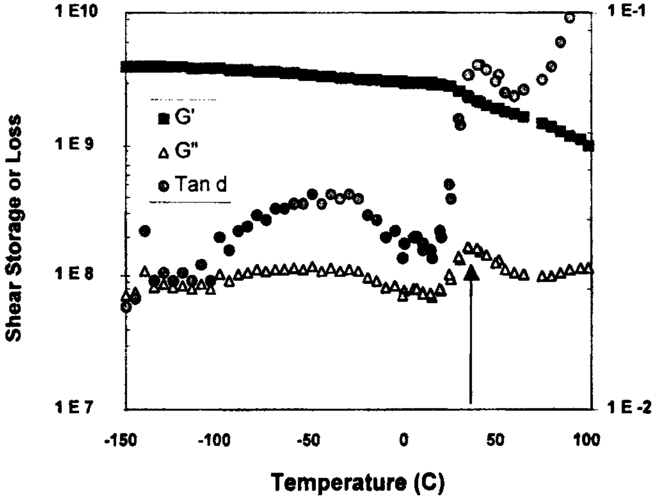

FIGURE 3. TATB dynamic mechanical response at 1-Hz showed two relaxations, a broad secondary with a maximum in the tan delta at about -45°C and a narrow secondary at about 34°C.

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 3, 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 coefficient[6] near this temperature.

Sub T_g Behavior

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 explosive[14] 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 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 4. All data shown in the figure were collected at 1 Hz. There could be several peaks hidden under this broad relaxation. In LX-17-1 with amorphous binder the maximum in the loss modulus occurred at -55°C, whereas in the crystalline samples it was slightly lower (-65 to -74°C) based on the observed peak. There also appeared to be a shoulder on this peak at about -85°C. When the maximum was determined by a second order polynomial fit to the data from -120 to 0°C, the fit peaks at temperatures about 5 to 10°C lower than the actual

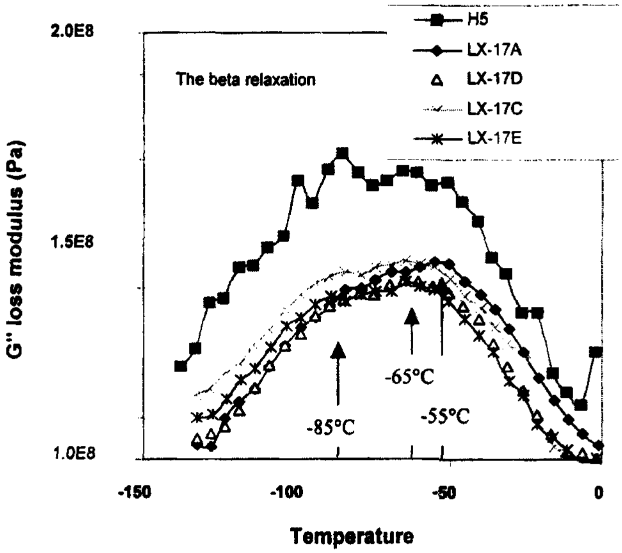

FIGURE 4. The β-relaxation appears as a peak (possibly 2 peaks) in the loss modulus at 1 Hz in LX-17-1 and varies slightly with explosive history.

maximum, but the amorphous relaxation was still about 5°C higher than the crystalline peak. The magnitude of the loss modulus (G") did not change substantially in any samples except the historical sample. Although the position of the maximum was effected by crystallinity, the magnitude of the loss modulus was not.

The loss tangent, shown in Figure 5, also passed through a maximum in this temperature region. The temperature of this peak was 5-10°C higher than the peak in the loss modulus. The amplitude of the loss tangent was also inversely dependent on binder crystallinity. This appears to be due to the storage modulus increase with increasing crystallinity. If G" is

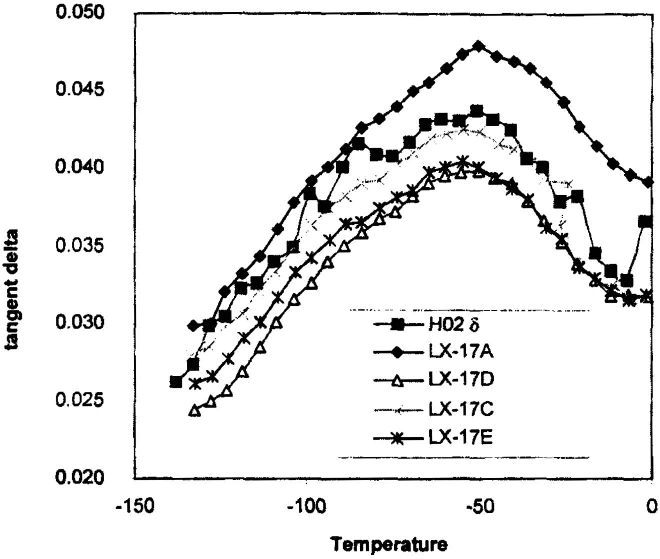

FIGURE 5. The tangent delta peak for the low temperature β relaxation occurs at a higher temperature than the G'' peak.

independent of crystallinity in this region and G' is directly related to crystallinity then tan δ should be inversely related since:

$$\tan \delta = G''/G' \qquad (6)$$

as was observed.

The temperature dependence of frequency, ω(T), in the β-relaxation usually follows an Arrhenius relationship:

$$\omega(T) = Ae^{-[E/RT(peak)]} \qquad (7)$$

Figure 6 shows several attempts to fit the maximum in the β-relaxation to equation 7. The activation energy was lower for tan delta than for the loss modulus. The fits were not especially good, probably due to the choice of 5°C as the temperature increment. The difference in maximum was about the order of the temperature increment, so an error in one measurement dramatically effected the accuracy of the fit. However, 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).

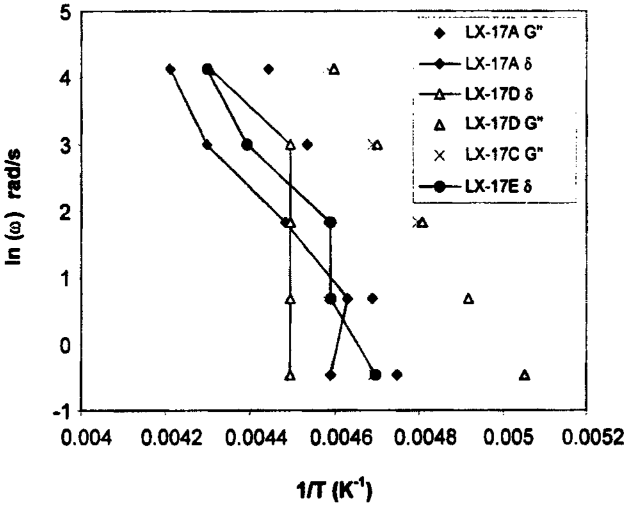

FIGURE 6. Frequency dependence of the β-relaxation gave an activation energy of 25 ± 5 kcal/mole based on G'' shifting and somewhat lower values for tan delta shifting.

2. Low Temperature Coefficient of Expansion: The RMS 800 maintains a constant tensile load on the specimen under test. As the temperature is increased, the sample expands and the length of the fixture is adjusted to restore constant load. The change in length is recorded and a linear expansion coefficient (LCTE or

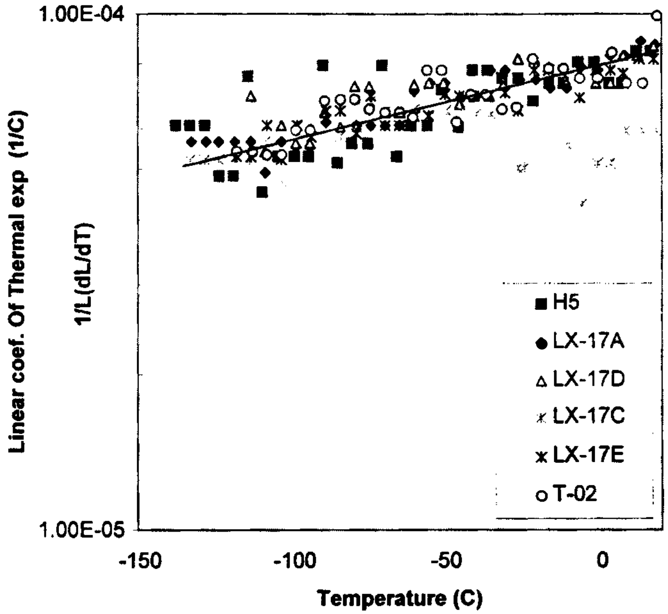

FIGURE 7. Sub T_g, LCST showed a direct correlation with temperature.

α_l) is calculated according to:

$$L_l = L_o(1 + \alpha_l \Delta T) \quad \text{or} \quad \alpha_l = (1/L_o)(\Delta L / \Delta T) \quad (8)$$

where L_o is the original length and L_l is the length after the change in temperature (ΔT). Below the glass transition the CTE should increase continuously with temperature[16]. Figure 7 shows the result from 6 sets of low temperature LCTE measurements from -140 to 20°C. With the exception of the LX-17-1C data, the thermal expansion coefficient below T_g seems to follow a linear increase with temperature of the form:

$$\alpha_l = mT + \alpha_o \quad (9)$$

Although the scatter is large for temperature T in degrees Kelvin, the average value of m was 1.93 E-7 with α_0 of 1.33 E-4. This slope is lower than the results of Maienschein and Garcia[17], which were measured from above T_g to 500°K, as would be expected for measurements below T_g. Stull and Ashcraft[18] measured the LCTE of LX-17-1 at -50, 15, 35 and 70°C. Their -50 and 15°C data are consistently less than ours are but the slope is the same within experimental error. Linear fits for each individual sample are given in Table 2.

TABLE 2. Coefficients of the temperature dependence of Sub T_g LCTE for LX-17-1 fitted to equation 9.

Sample	Slope	α_0(C)	α_0(K)	r^2
LX-17A	2.20E-7	8.05 E-5	1.41E-4	0.8793
LX-17B	1.98E-07	8.39E-5	1.35E-4	0.8380
LX-17C	1.55E-7	7.41E-5	1.23E-4	0.0316
LX-17D	1.76E-7	7.92 E-5	1.29E-4	0.6803
LX-17E	1.87 E-7	7.66 E-5	1.32E-4	0.8238
T-02 SRR	2.04 E-7	7.93 E-5	1.36E-4	0.6558
T-04 SRR	1.66E-7	7.69E-5	1.26E-4	0.6292
H2	3.19E-7	8.33E-5	1.68E-4	0.5739
H5	1.79 E-7	7.70 E-5	1.29E-4	0.5010

3. *Low temperature shear storage modulus:* If the effect of the β-relaxation and frequency dependence are neglected, the shear storage modulus (G') below T_g can be fitted to a simple linear temperature dependence of the form[19]:

$$G'_1 = c\Delta T + G'_0 \qquad (10)$$

or

$$\log G'_1 = K\Delta T + \log G'_0 \qquad (11)$$

where c and K are the temperature coefficient of the low-temperature shear storage modulus and G'_1 and G'_o are shear storage moduli at T_1 and T_o. In Figure 2 the dotted line approximates the fit of equation 11 to a single frequency data set of G' versus T values. The fit is reasonable up until the glass transition where the storage modulus drops off dramatically in amorphous LX-17-1. Table 3 shows the fits of equations 10 and 11 to 5 frequencies of low temperature data. Equation 11 yielded a slightly better fit. Since there is no frequency dependence in either equation, the fits to all frequencies are not expected to be very good. An attempt to time-temperature super impose the low temperature data from all 5 frequencies around the β-relaxation of G' resulted in poor fits for tan delta and G" in the low temperature/high frequency part of the curve. Apparently time-temperature shifting is inappropriate for this temperature/frequency regime[11,20].

The Glass Transition of the Binder

1. *Vitrification of KF-800:* 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 8 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

TABLE 3. Sub T_g shear storage modulus fits to equations 10 and 11 show temperature dependence of G' is reasonably log linear.

Sample	Slope	intercept	G'(0°C) GPa	R^2	ρ_o
LX-17A	-9.92E-4	9.4248	2.66 ± 0.03	0.963	
A linear	-7.15E7	2.64E10		0.8886	
LX17B	-1.08E-3	9.473	2.97 ± 0.05	0.982	1.878
B linear	-8.54E7	2.96E10		0.9778	
LX17C	-9.34E-4	9.486	3.06 ± 0.06	0.974	1.911
C linear	-2.43E6	2.63E9		0.9694	
LX17D	-1.08E-3	9.490	3.09 ± 0.07	0.9794	1.902
D linear					
LX17E	-9.97E-4	9.489	3.08 ± 0.02	0.977	1.910
E linear	-7.95E7	3.08E10		0.9709	
T-02 SRR	-1.09E-3	9.487	3.07 ± 0.07	0.981	
T-02 linear	-1.06E7	2.985E10		0.9813	
T-04 SRR	-1.19E-3	9.527	3.37 ± 0.10	0.982	
T-04 linear	-7.95E7	3.08E10		0.9709	
H2*	-9.79E-4	9.553	3.57 ± 0.04	0.996	
H2 linear	-9.79E7	3.57E10		0.9916	
H5*	-9.37 E-4	9.523	3.34 ± 0.05	0.991	
H5 linear	-9.37E7	3.34E10		0.991	

*data for 1 Hz fit only data.

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, discussed below. The shear storage modulus of LX-17-1 with partially crystalline binder approaches 0.7 GPa as the crystals melt with increasing temperature. The shear storage modulus is not constant below T_g as seen in the figure. This also appears to correlate with the degree of crystallinity, but may be due to densification in the weapon or other physical aging processes.

The peak in the shear loss modulus (G'') was consistent with the glass transition temperature of the binder[3]. In all the LX-17-1 samples tested, this peak occurred at 30 ± 2°C at 1

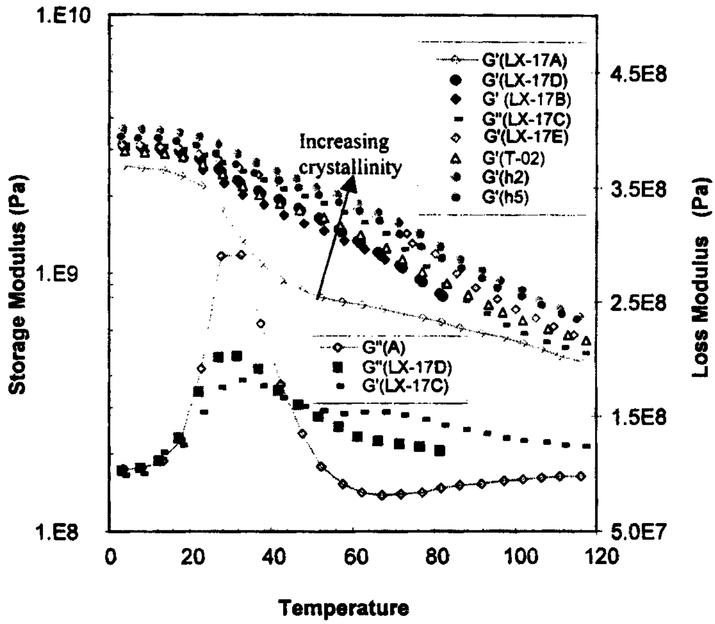

FIGURE 8. The shear storage modulus (G') of LX-17-1 with semi-crystalline binder was 3 GPa compared to 0.7 GPa for amorphous binder above T_g (from 40 to 90°C)

Hz. In Figure 9 the loss modulus at 1 Hz for various LX-17-1 samples corresponding to the storage modulus data in Figure 8 showed no evidence of plasticization (T_g shifted downward in temperature compared to pure binder) or anti-plasticization (T_g increasing with filler). The glass transition at 1 Hz in KF-800 lot 629[3] 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

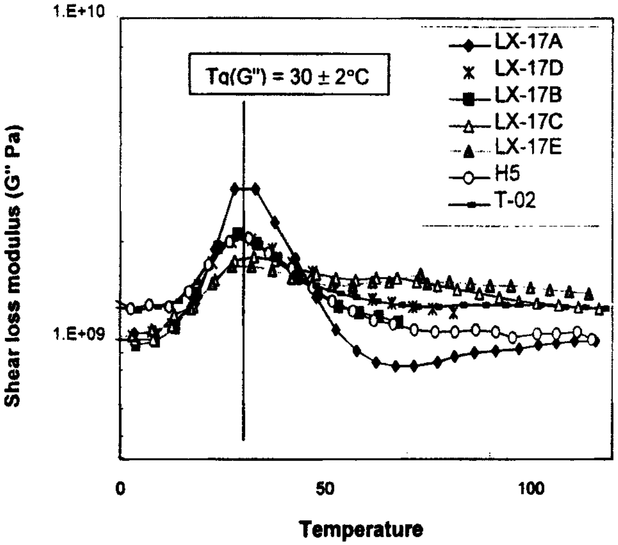

FIGURE 9. Based on the maximum in G'', the glass transition temperature of the binder in LX-17-1 from different samples varies only by about ± 2°C.

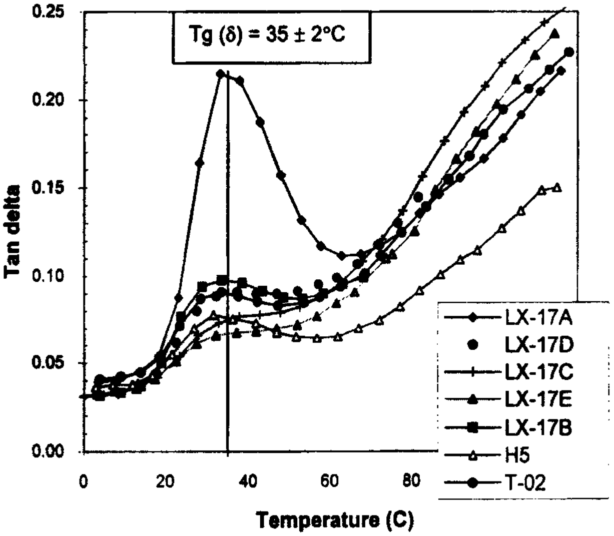

FIGURE 10. The tangent delta T_g is higher than the loss modulus.

peak while the stockpile returns gave the least. The peak baseline below T_g, that 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 magnitude of the loss modulus above the transition follows the relationship: G"{Thermal cycled (B)} ≅ G"(historical) < G"(SRR) ≅ G"(ambient) < G"(9 and 10 yr. stockpile). This is consistent with a varying degree of crystallinity in these samples as discussed in section 3.

The peak in the tan delta trace associated with the glass transition, shown in Figure 10, occurred about 35 ± 2°C and the transition temperature is independent of crystallinity or other treatment. The intensity of the tan δ peak for LX-17-1 followed the degree of crystallinity of the binder, i.e., amorphous binder > thermal cycled > 8 yr. ambient ≅ SRR > stockpile 9 yr. > stockpile 10 yr. Note that the baseline of the tan delta relaxation 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.

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 range[20]. For a wide variety of amorphous polymers, the amount of shift has been shown to follow the WLF relationship:

$$\log a(T) = [C_1(T - T_r)]/[C_2 + T - T_r] \qquad (12)$$

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 11. C_1 and C_2 are constants. When the data for LX-17-1A were shifted about T_r of 32.5°C, C1 and C2 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 12 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.

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

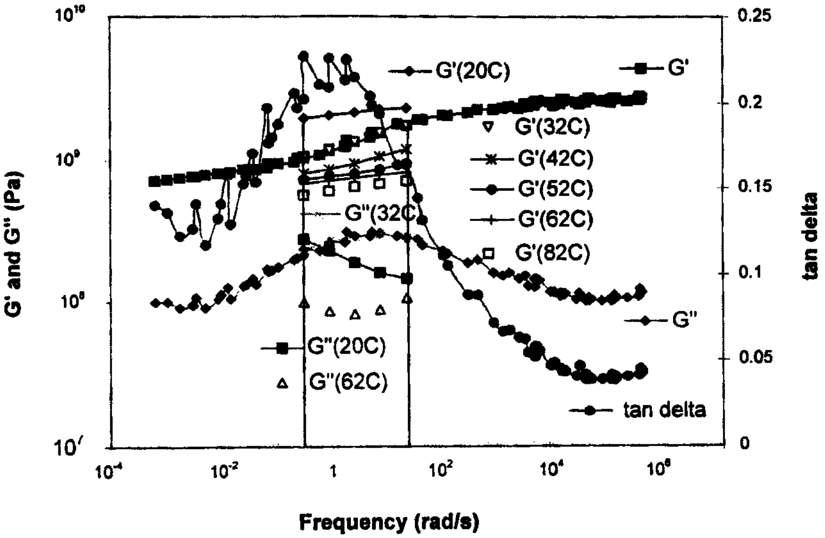

FIGURE 11. Data from LX-17-1A (amorphous) measured over 2 decades of frequency at various temperatures can be shifted about 32°C to cover 12 decades.

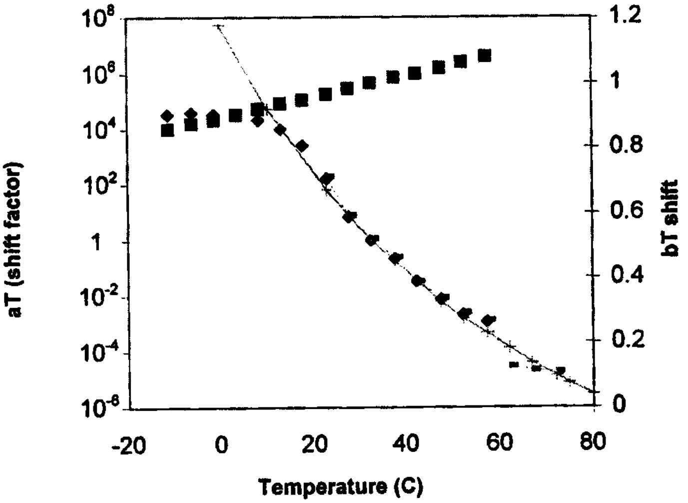

FIGURE 12. Shifting behavior for LX-17-1A (amorphous binder) can be modeled by WLF relationship over the temperature range from 20 to 80°C.

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 2 (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 8. Amorphous KF-800 in LX-17-1A should serve as a baseline for comparison. The thermal cycled sample (B) has the lowest shear storage modulus, consistent with the lowest degree of crystallinity. This is probably due to the slow growth rate of KF-800 crystals at 70°C and melting of less perfect crystals during the high temperature thermal cycle. Sample D was stored at ambient as a core test control. No record of the exact temperature seen by this sample was available, but it is assumed that near the glass transition temperature, crystals grow slowly. Note that the modulus of sample B flattens out and follows sample D above about 60°C. This is probably because the less perfect crystals formed at ambient have been melted out of sample D and above 60°C, the crystallinity of the two samples were comparable. Unfortunately, both these samples broke at 81°C. Sample C and E are the 9 and 10 year stockpile samples, respectively. They have higher crystallinity because nuclear material in the vicinity of the explosive increases the temperature of its environment to slightly above T_g. The shear storage modulus of samples C and E seem to approach the values of D and B above 80°C. This is associated with the temperature that LX-17-1 was exposed to during its lifetime. 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.

Modulated differential scanning calorimetry (MDSC) was run on several of the LX-17-1 samples. Although the heats of fusion obtained from the melting endotherms are near the limit of the instrument resolution, the trend is similar to that observed in the dynamic mechanical properties. Table 4 gives the heats of fusion (ΔH_f), degree of crystallinity (X_c), and the peak in the melting endotherm (T_m) from 20-mg samples of explosive. These data showed:

$X_c(A) < X_c\ (B \approx D \approx E) < X_c\ (C)$ and

$T_m(B) > T_m\ (C \approx E) > T_m(D)$

consistent though not identical with dynamic mechanical results. It should be noted that because of the small differences in ΔH_f, the values of X_c should only be interpreted as trends and not exact values. However the melting peak data is consistent with what is known from stockpile and storage information and with crystallinity behavior in polymers.

TABLE 4. MDSC results of several LX-17-1 samples were machined from the same test components as were used for dynamic mechanical analysis.

Sample	ΔH_f (j/g)	sd	X_c (%)	sd	T_m (°C)	sd
LX-17-1A	0					
LX-17-1B	0.115	0.02	3.2	0.5	96.9	1.0
LX-17-1C	0.16	0.04	5.0	1.0	81.3	0.2
LX-17-1D	0.11	0.02	3.5	0.5	72.4	0.3
LX-17-1E	0.115	0.02	3.7	0.6	81.6	1.0
H5	0.147		4.3		75.2	0.4
LX-17-1 mp2*	0.065	0.02	1.9	1.0	72.6	1.2

• Data was from molding powder of historical lot from which billet H2 was pressed.

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. Figure 13 showed the result of shifting G' and G'' with frequency based on optimized shift factor for tangent delta for LX-17-1E. Clearly, 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.

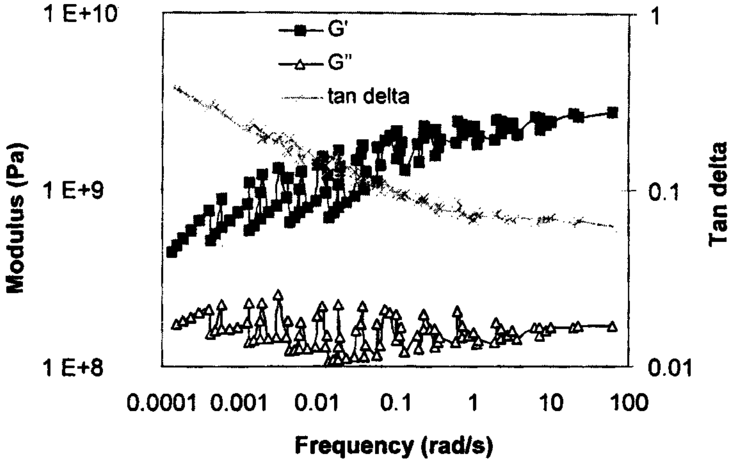

FIGURE 13. Unfortunately data from LX-17-1E or other samples with some binder crystallinity measured over two decades of frequency at various temperatures cannot be shifted with consistent results for all dynamic mechanical functions.

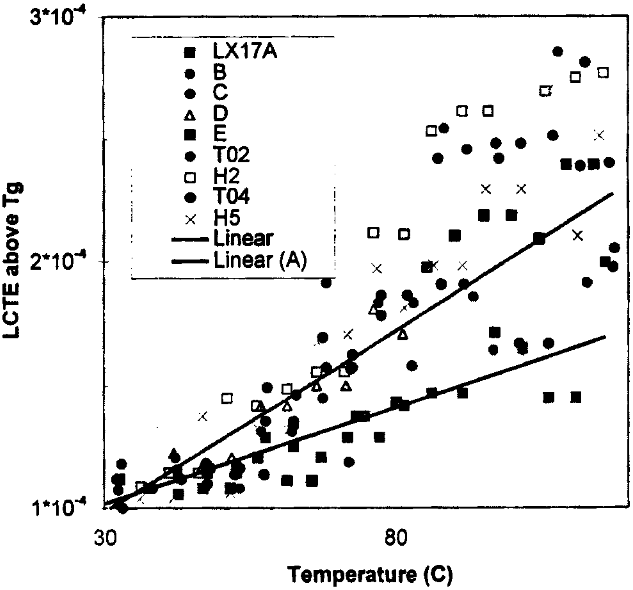

FIGURE 14. LCTE above the glass transition is higher for LX-17-1 with crystalline binder than for amorphous binder.

4. Thermal expansion above the glass transition. The coefficient of thermal expansion above T_g should be greater than sub-T_g CTE. Results for LX-17-1 in Figure 14 showed higher LCTE for the above T_g measurements compared to those in Figure 7. Values below T_g varied from 0.00005 to 0.00008 $°C^{-1}$ at -130 and 0°C, respectively. Values above T_g varied from 0.0001 to 0.00015 $°C^{-1}$ at 30 and 100°C, respectively. The data of Stull and Ashcroft[18] was considerably lower than our data, but axial expansion data measured by Maienschein and Garcia[17], fell almost exactly on the amorphous results given in Table 5. Contrary to what would normally be expected, the LX-17-1 with some degree of crystallization in the binder gave a higher LCTE (0.00027 $°C^{-1}$) than the amorphous binder LX-17-1. The expansion of semicrystalline KF-800 is expected to be less than for rubbery KF-800. Maienschein and Garcia also saw unusual behavior in samples pressed at elevated temperatures. This is may be due to reduced irreversible growth of the TATB by crystalline KF 800.

TABLE 5. Crystalline samples had higher Linear CTE data above T_g (30>T>115°C) than amorphous LX-17-1(A).

Sample	Slope	Intercept	r^2
Amorphous	7.89E-07	7.80E-05	0.776
LX17B	1.42E-6	5.53E-5	0.9033
LX17C	1.974E-6	3.20E-5	0.8442
LX17D	1.44E-6	5.54E-5	0.9015
LX17E	1.923E-6	1.56E-5	.896
T-02 SRR	1.52E-6	4.88E-5	0.6344
T-04 SRR	1.52E-6	4.92E-5	0.7480
H-02	2.50E-6	1.15E-5	0.9354
H-05	1.92E-5	3.17E-5	0.9187

CONCLUSIONS

Three relaxations were found in the dynamic mechanical properties of LX-17-1. The β-relaxation occurred at -65°C in LX-17-1, about 15°C lower than in either the binder or pure TATB. Its maximum was influenced by the crystallinity of KF-800. The glass transition in LX-17-1 was observed at the same temperature as KF-800 (30-32°C). 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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