LA-UR-99-3304

Title:

EFFECTS OF TEMPERATURE, PRESSURE, AND AGING ON THE POLYMER TRANSITIONS OF PLASTIC BONDED EXPLOSIVES

Author(s):

M. S. Campbell and D. A. Garcia

Submitted to:

http://lib-www.lanl.gov/la-pubs/00796362.pdf

EFFECTS OF TEMPERATURE, PRESSURE, AND AGING ON THE POLYMER TRANSITIONS OF PLASTIC BONDED EXPLOSIVES

M. S. Campbell and D. A. Garcia, Los Alamos National Lab, Los Alamos, NM
mscampbell@lanl.gov

ABSTRACT

Plastic bonded explosives (PBX) contain 5-wt% polymer, plasticizer, and stabilizer as binder. The temperature of the glass transition (T_g) determines if the binder will reduce or increase the sensitivity of the PBX to impact. A soft polymer, such as Estane, a polyester/polyurethane block polymer with T_g below the temperature of use, reduces the sensitivity; however, it must retain the mechanical strength necessary for dimensional stability throughout processing and its lifetime. One binder studied was 50-wt% Estane and 50-wt% plasticizer. Glass transitions and other polymer relaxations were found by temperature modulated DSC for PBX before and after pressing at 90°C, which is above the softening temperature of the binder; and for Estane and PBX under aging conditions. PBX prepared with aged Estane was also tested for changes in the binder T_g.

INTRODUCTION

Crystalline explosives are combined with a polymeric binder to formulate composite plastic-bonded explosives (PBXs). These materials can be pressed into billets and machined for use in explosive devices. The purpose of this study is to measure T_g and other thermal properties of PBXs, their binders, and polymers at different stages in processing and storage.

1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane (HMX) requires a rubbery binder to cushion it from accidental stimuli such as the friction and shock of dropping a billet on a rough surface (*1*). For these materials it is desirable to use a polymeric binder, which has a T_g below the temperature of use, for reliable desensitization. The binder also needs strength to achieve the desired mechanical behavior of the PBX. To achieve both these ends, Estane, a block-polymer made from a combination of soft segments and hard segments bonded by ester and urethane linkages (*2*), is plasticized by a energetic plasticizer, which is the eutectic of bis(2,2-dinitropropyl)acetal and bis(2,2-dinitropropyl)formal, known as nitroplasticizer (NP). The addition of NP lowers the T_g to –50°C and contributes to the overall release energy of the PBX upon detonation.

EXPERIMENTAL

Equipment

The T_g and endothermic polymeric relaxation data were obtained using the modulated option on TA Instruments Differential Scanning Calorimeter 2920

(MTDSC). Unlike the traditional DSC, which can not distinguish complex transitions that occur in the same temperature range, the use of the MTDSC separates the total heat flow signal into its heat capacity and kinetic components. The glass transition is a reversible, heat capacity change but endothermic polymer relaxation is a non-reversible change. The electronics and software separate the total heat flow, which has a superimposed sinusoidal temperature variation, into the reversible and non-reversible heat flow traces. The TA Instruments DSC 2920 uses a nitrogen gas purge and liquid nitrogen-cooling accessory for sub-ambient and modulated analyses. The cell measures differential heat flow between sample and inert reference pans on raised platforms on a constantan disk. The differential heat flow is monitored by thermocouples welded to the disk. The sensitivity is 0.2 μW, and temperature repeatability is 0.10°C.

Sample Preparation:

Approximately 18-mg samples were pressed into crimped aluminum sample pans in the TA Instruments Sample Press. The reference sample contained an equal amount of glass beads and was prepared in the same manner as the sample. The weights of the sample and reference pan were within ~0.5 mg.

Analysis Program

Computer control of the temperature was important to prevent an explosive sample from reaching its runaway explosion temperature.
The following method was run for each sample containing Estane:

Equilibrate at -74°C
Modulate at +/-1.000°C every 60 seconds
Isothermal for 4 minutes, Data storage on.
Ramp at 2°C/min to 120°C, Data storage off, Cool 50°C.

Materials Processing

The slurry process is used to formulate PBX 9501. The crystalline explosive HMX is slurried in water and binder is dissolved in methyl ethyl ketone (MEK), which is not miscible in water. After the binder solution is added, the mixture comprised of solid plus two liquid phases is turbulently mixed. The MEK-rich phase is removed by distillation to achieve a single liquid phase system in which small beads of PBX are insoluble. The PBX is filtered and dried at 60°C. Molding powder-containing HMX is heated up to 90°C before pressing. Pressed billets are machined to desired shape. Compression-molded Estane is pressed at 110°C between Teflon sheets. Storage was at ambient or elevated temperature.

Gel Permeation Chromatography

The molecular weights of the Estane samples were compared with polystyrene standards in THF solution on a Waters GPC with a refractometer.

RESULTS AND DISCUSSION

The glass transition of a highly filled polymer can be seen by MTDSC if the glass transition is such that its change in heat capacity is large enough to be seen above the noise. The T_g of a filled polymer is confirmed by the minimum of the derivative of the reversible trace in the temperature region of the T_g. Softening of the soft segment and the glass transition of the hard segments are in a similar temperature range for Estane. The derivative of the reversible trace was used to differentiate between melting and glass transitions.

Estane 5703

Hydrolysis at the ester linkages or radical attack at the urethane linkage (*3*) can cause changes in molecular weight of Estane exposed to the atmosphere. To answer the question whether accelerated aging produced the same changes in the soft segment T_g as the Estane aged at ambient temperature, first the T_g of older samples of Estane, which were stored under ambient conditions for up to 17 years, were plotted against M_w. Fig. 1 compares the T_g with the M_w data for 13 samples. Second, samples were placed in an oven at 70°C and 75% relative humidity for 2, 3, and 5 weeks. Table I shows the T_g's of the amorphous soft and hard segments of the Estane after elevated temperature aging as well as the calculated soft segment T_g determined from the equation from Fig. 1 of aged Estane. All the naturally aged Estane had a lower T_g's than the artificially aged Estane for the soft segment implying that the oligomers formed in natural aging were better plasticizers of the Estane. Perhaps the mechanism is different. The hard segment T_g shows a sharp drop of about 20°C in the T_g from new to aged samples but no linear relation with the Mw. Whatever caused the drop does not lower the T_g proportional to the amount as is seen in plasticizer addition.

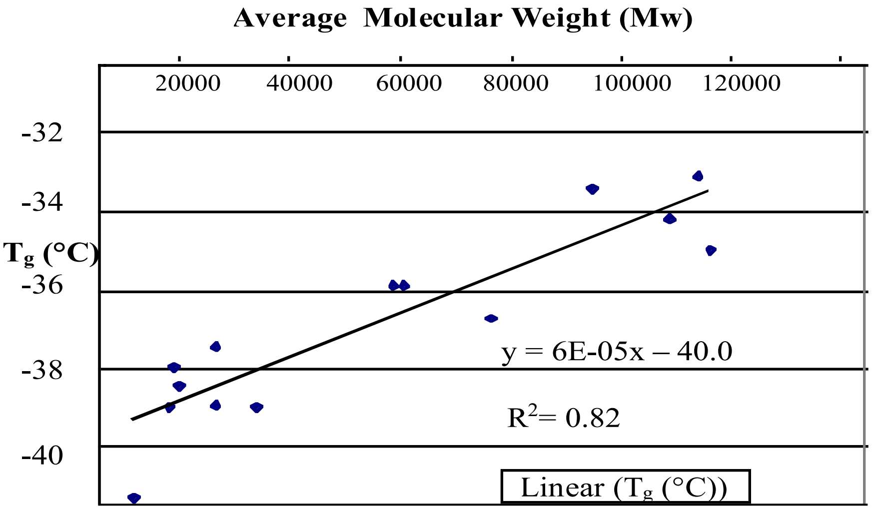

Fig. 1. The soft-segment T_g has a linear relation with the M_w.

Binder of PBX 9501

The PBX 9501 binder is a 50/50-wt% mixture of Estane and NP. This more flexible mixture has a T_g of –50.3 °C for the soft segment and 50.1°C for the amorphous part of the hard segment. The hard segment is more crystalline than the soft segment; therefore, the heat capacity change is very small, about 0.03 J/g/°C hence below detection in the PBX. Figure 2 shows the MTDSC scan for the binder. The reversible heat flow shows the T_g's and the nonreversible heat flow shows the two endothermic relaxations of the binder related to the T_g's.

PBX 9501

PBX 9501 is 95-wt% HMX and 5-wt% binder. The soft-segment glass transition has a heat capacity change of 0.3 J/g/°C, which is large enough to be seen easily in the PBX. The T_g of the PBX is about the same as the binder. The T_g did not change after pressing at 90°C and 30 kpsi (Table II). The hard segment T_g was not seen above the noise. Pressed PBX 9501 aged for 16.7 years under inert atmosphere at ambient temperature was machined into chips and tested for change in T_g. Table II also compares the aged T_g data with its original molding powder T_g and a recently pressed sample from the molding powder T_g.

Table I. Relation of T_g to M_w

Sample	Soft Segment T_g,C_p (°C, J/g/°C)	Hard Segment T_g,C_p (°C, J/g/°C)	M_w KDaltons
Pellet Estane	-33.0, 0.34	49.9, 0.056	117
Compression	-32.0, 0.35	52.9, 0.050	117
Calc T_g	-32.6		117
Aged 2 wk	-33.2, 0.38	33.7, 0.012	88
Calc, T_g	-34.6		88
Aged 3 wk	-34.8, 0.32	31.1, 0.029	64
Calc, T_g	-36.3		64
Aged 5 wk	-36.1, 0.35	31.6, 0.011	43
Calc, T_g	-37.7		43

Another aged sample had a T_g of –45.4°C, but it may have been due to migration of plasticizer away from the area. When an equation for change of T_g with amount of NP, $T_g = -7.11 \times (\text{wt\%NP}) - 32.7$, was used to adjust T_g for aged samples, the NP-depleted aged sample was found to have the same T_g as the original molding powder, –50.1°C (*4*).

After a PBX is stored in a warm humid environment, its Estane would be hydrolyzed; and properties determined by its average molecular weight would change. A batch of PBX 9501 was made from Estane that was artificially aged and the T_g of this PBX is also included in the Table II. There seems to be a trend toward lower T_g with the time the Estane was aged.

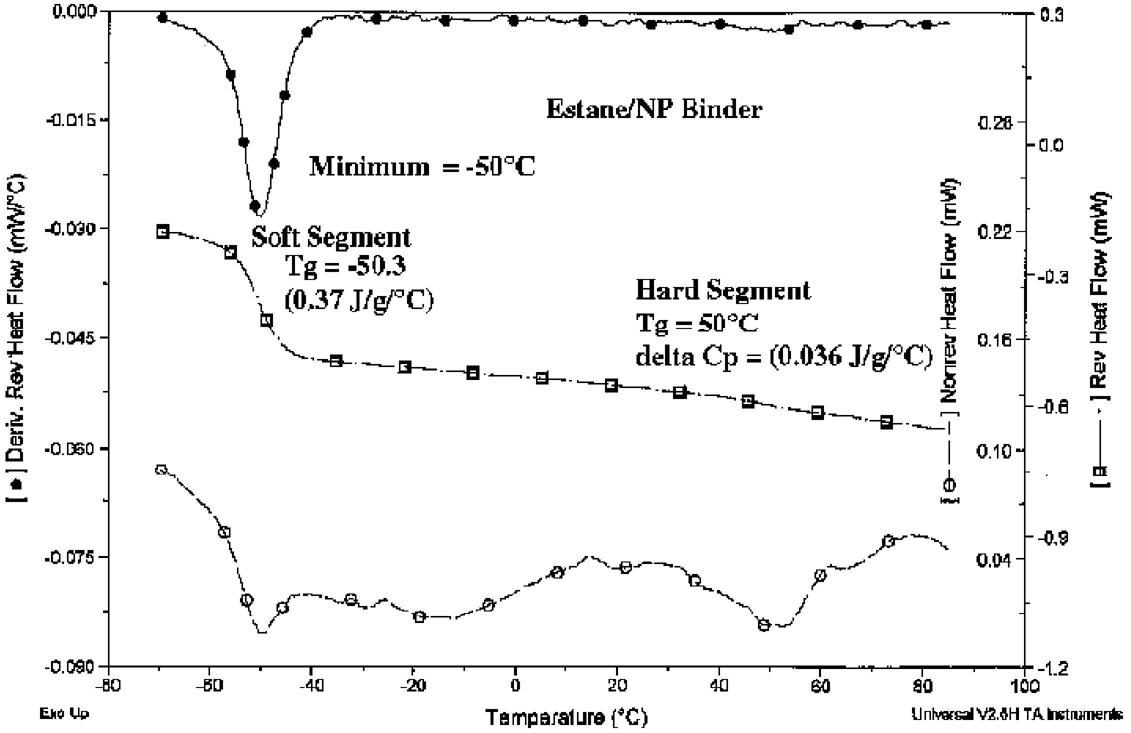

Fig. 2. MTDSC analysis of the binder of PBX 9501 shows the reversible, its derivative, and nonreversible thermal transitions.

Table II. Soft Segment T_g of PBX 9501 after Processing and Aging

Material	Sample Condition	T_g (°C)
PBX 9501		
Lot 730-004	Molding Powder, 17 y in ambient condition	-49.7
Lot 730-004	Pressed at 90°C, cooled 2 h	-49.3
Lot 730-004	Pressed and aged 16.7 y in inert atm.	-46.8
Lot 730-010	Molding powder, 10 y in ambient conditions	-48.3
Lot 730-010	Pressed at 90°C, cooled 2 h	-48.0
Lot 730-006	Pressed and aged 14 y inert atm. adjusted wt% NP	-50.1
Batch 7278	New Batch molding powder with new Estane	-45.4
Batch 7284	Batch with Estane aged 2 wk, 70°C, 75% Rel. Hum.	-45.9
Batch 7279	Batch with Estane aged 3 wk, 70°C, 75% Rel. Hum	-47.5
Blend 99-1	Blend with Estane aged 5 wk, 70°C, 75% Rel. Hum	-48.4

CONCLUSIONS

The data suggest that the glass transition temperature of the Estane is lowered by addition of the plasticizer, but not affected by addition of HMX. It remains at about –49°C. The results also show that pressing does not change the soft segment T_g very much. Aging affects the soft segment T_g in the same way as a plasticizer because hydrolysis of the ester linkages can produce fragments that behave as plasticizers for the soft segment. An aged sample with low NP was found to have a higher T_g, but it was due to loss of some of the NP by migration. New PBX 9501 batches, which were made with aged Estane, show a trend toward lower T_g. The variations in T_g result from sampling and noise because of the low percentage of binder in PBX 9501. Future work will average several sample analyses. In addition, the fragments of hydrolysis from Estane aged at ambient temperature and at elevated temperature that could be causing plasticization of the Estane will be identified.

ACKNOWLEDGMENTS

Thanks to Wayne King for GPC analysis of the Estanes.

This work was performed under the auspices of the U.S. Department of Energy.

REFERENCES

1. Gibbs, T. R.; Popolato, A. *LASL Explosives Property Data*; University of California Press: Berkeley, 1980, p 454-457.
2. B. F. Goodrich Co., Estane 5703 Product Data Sheets. And B. F. Goodrich Specialty Chemicals, TSR 76-02 TF116, March 1995.
3. Jellinek, H. H. G.; Wang, T. J. Y.; *J. Polym. Science, Polym. Chem. Ed.*, **1973,** *11*, 3227.
4. Garcia, D. A.; Campbell, M. S.; Los Alamos National Laboratory report, LA-UR-99-2535, May 1999.