ELSEVIER

Thermochimica Acta 357–358 (2000) 89–95

thermochimica acta

www.elsevier.com/locate/tca

Effects of temperature and pressure on the glass transitions of plastic bonded explosives

Mary Stinecipher Campbell*, Danielle Garcia, Deanne Idar

MS C920, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Received 15 September 1998; accepted 28 January 1999

Abstract

Various plastic bonded explosives (PBXs) contain about 5 wt.% polymer, plasticizer, and stabilizer as binder. The glass-transition temperature (T_g) determines, in part, if the binder will reduce or increase the sensitivity of the PBX to impact. A soft binder reduces the impact sensitivity; however, too soft a binder compromises the mechanical strength below that desirable for dimensional stability. Glass transitions were measured by temperature modulated DSC for PBXs before and after pressing. Pressing temperature was 90°C. The T_g of Estane, a polyester/polyurethane used in some PBX binders, was investigated. Only small changes were observed in the low temperature T_g of the soft segments but larger changes were seen in the higher temperature transitions due to the relaxation of the hard segments. The T_g of Kel F 800, a binder used in insensitive PBX 9502, was observed near ambient temperature. The PBX 9502 had a lower T_g than the neat polymer. Mechanical strength was measured for the samples of PBX 9502. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: PBXs; Kel F 800; Nitroplasticizer; Estane; Glass-transition temperature (T_g); HMX; TATB

1. 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 testing and 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. Quasi-static low-strain rate compression measurements are compared with the measured T_gs to determine if the change in the T_g can be used as an indication of a significant change in physical properties.

We measured the thermal properties of two different PBXs. The more insensitive explosive, PBX 9502, is formulated with 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) bonded with Kel F 800, a chlorotrifluoroethylene/vinylidine fluoride copolymer manufactured by 3M. Kel F is very thermally and chemically stable, has good mechanical properties at ambient temperatures and melts at about 100°C, which is the pressing temperature for the PBX 9502.

The more sensitive explosive 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) requires a more 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 with 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

* Corresponding author.

PII: S0040-6031(00)00372-5

urethane linkages [2], is plasticized by the energetic plasticizer BDNPA-F[50/50 wt.% eutectic of bis(2,2-dinitropropyl)acetal/bis(2,2-dinitropropyl)formal], also known as nitroplasticizer (NP). The addition of NP lowers the T_g and contributes to the overall release energy of the PBX upon detonation.

2. Experimental

2.1. Equipment

The T_g and the endothermic polymeric relaxation data were obtained using the modulated option on TA Instruments Differential Scanning Calorimeter 2920 (M-DSC)^{TM}. Unlike the traditional DSC, which cannot distinguish complex transitions that occur in the same temperature range, the use of the M-DSC 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 DSC 2920 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 DSC 2920 uses a nitrogen gas purge and liquid nitrogen-cooling accessory for sub-ambient and modulated analyses. The DSC 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.

2.2. Sample preparation

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

2.3. Analysis program

Computer control of the temperature was important to prevent an explosive sample from reaching its runaway explosion temperature, which might damage the DSC cell.

The following method was run for each sample containing Estane:

Equilibrate at −74°C
Modulate at +/−1.000°C for every 60 s
Isothermal for 4 min
Data storage: on
Sampling interval: 1.0 s/pt
Ramp at 2°C/min to 120°C
Data storage: off
Equilibrate at 50°C

Kel F containing samples were tested with a similar method except cooled to −30°C.

2.4. Materials processing

The slurry process is used to formulate PBX 9501 and PBX 9502. The crystalline explosive is slurried in water and binder is dissolved in an organic solvent, 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 second solvent phase is removed either by distillation or addition of water to achieve a single liquid phase system in which small beads of PBX are insoluble. The crystalline explosive, covered by the binder in this manner, is called molding powder. The molding powder is filtered off, dried, and pressed. Molding powder containing HMX is heated up to 90°C before pressing, while that containing TATB is heated to 100°C. Pressed billets are machined to desired shape using water for cooling the cutting surface. Usual storage is in magazines under ambient temperature and atmosphere, but accelerated aging studies have used inert gas and selected temperatures.

In the case of PBX 9502, a variation on the above procedure was used to reduce waste. The slurry mixture contained both crystalline TATB with the required amount of Kel F and 50 wt.% from the machining scrap from previously processed PBX 9502. It is unknown how much of the previously processed Kel F went back into solution. This molding powder was designated recycled PBX 9502 to differentiate it from the virgin PBX 9502 prepared in the normal manner. Mechanical and thermal analysis specimens were obtained from samples that were pressed and

machined between the years of 1985 and 1989 and stored under ambient temperatures.

2.5. Quasi-static, low strain rate compression tests

The PBX 9502 specimens were machined as 1.0 in. diameter, 1.0 in. length right circular cylinders. Specimens were tested at ambient temperature and humidity using an Instron 1123 Materials Testing Workstation with 6.0 in. diameter compression anvils, a 5000 lb maximum load cell, and an extensometer gauge to measure strain. Load and extensometer voltage measurements were recorded with an oscilloscope. Digitized data were acquired using GPIB interface macros written in Igor Pro and loaded on a Macintosh Powerbook. Every specimen was tested on the 5000 lb load range with a 0.05 in./min crosshead speed at an approximate strain rate of $0.0083\ s^{-1}$. Anvils were lubricated with Dow Corning 321 Dry Film Lubricant and allowed to dry and specimen ends were lubricated with Dow Corning Molykote 33 grease applied to the specimen ends just prior to testing [4].

2.6. Gel permeation chromatography

The molecular weights of the Estane samples were found by running a THF solution on a Waters GPC using a refractometer detector and compared with polystyrene standards.

3. Results and discussion

The glass transition of a highly filled polymer can be seen with by M-DSC if the glass transition is such that its change in heat capacity is large enough to be seen above the noise. The Estane soft segment T_g is easier to detect than Kel F 800 because it is less crystalline. Even though the heat capacity change is low in the PBX with Kel F, we are able to measure the T_g change in the filled polymer on both by confirming the T_g inflection with the minimum of the derivative of the reversible trace in the temperature region of the T_g. Melting of the soft segment and glass transition of the hard segments are in similar temperature range for PBX 9501; therefore, again the derivative of the reversible trace was used to differentiate between melting with negative and positive inversion points and glass transition with only a negative inversion.

3.1. Estane 5703

We found the glass transition of some older samples of Estane had shifted to a lower temperature as a function of the molecular weight changes. The samples had been stored under ambient conditions for up to 17 years. Changes in molecular weight of Estane exposed to the atmosphere can be caused by hydrolysis at the ester linkages or radical attack at the urethane linkages [3]. The shift in T_g was a linear relation with the weighted average molecular weight of the Estane found by gel permeation chromatography (GPC). Lower molecular weight oligomers may have acted like plasticizers to lower the T_g. Fig. 1 compares the T_g with the M_w data for 13 samples.

The sample used for the pressing study had been removed from the freezer and exposed to ambient conditions for a few months. It had a M_w of 111,000 Da. Its soft segment T_g was not affected by heating to 60°C for drying or heating to 90°C and pressing; however, the endothermic heat of polymeric relaxation at 40°C is reduced after these processes and its onset moved to lower temperatures, Fig. 2. The time at ambient temperature after these processes was several months in the case of the drying but only a day for the pressed material. A second run of the same pressed sample returned the endothermic heat to previous levels.

3.2. Binder of PBX 9501

The PBX 9501 binder is a 50/50 wt.% mixture of Estane and NP. This more flexible mixture has a lower T_g of −50°C. Fig. 3 shows the M-DSC scan for the binder. The nonreversible trace shows an endothermic relaxation of the binder with very little reversible melting at 35°C.

3.3. PBX 9501

PBX 9501 is 95 wt.% HMX and 5 wt.% binder. The T_g of the PBX is about the same as the binder alone. We are studying the effect of normal processing on the

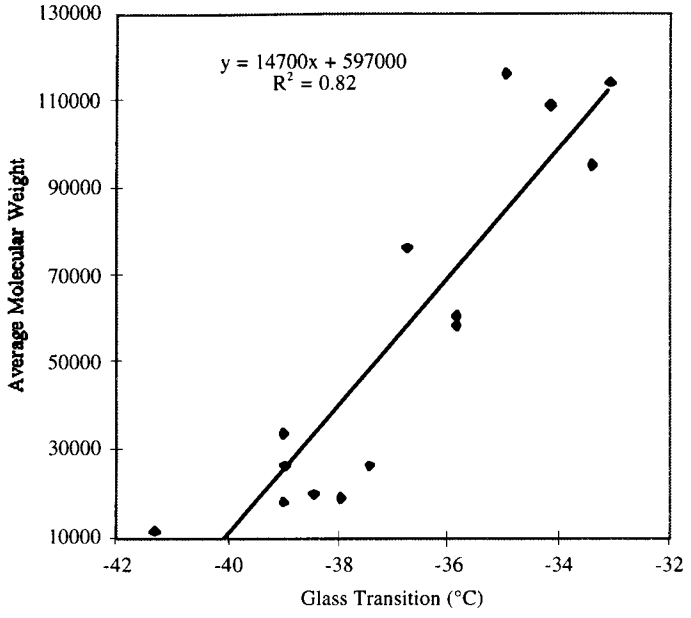

Fig. 1. Aged Estane with a lower M_w has a lower T_g.

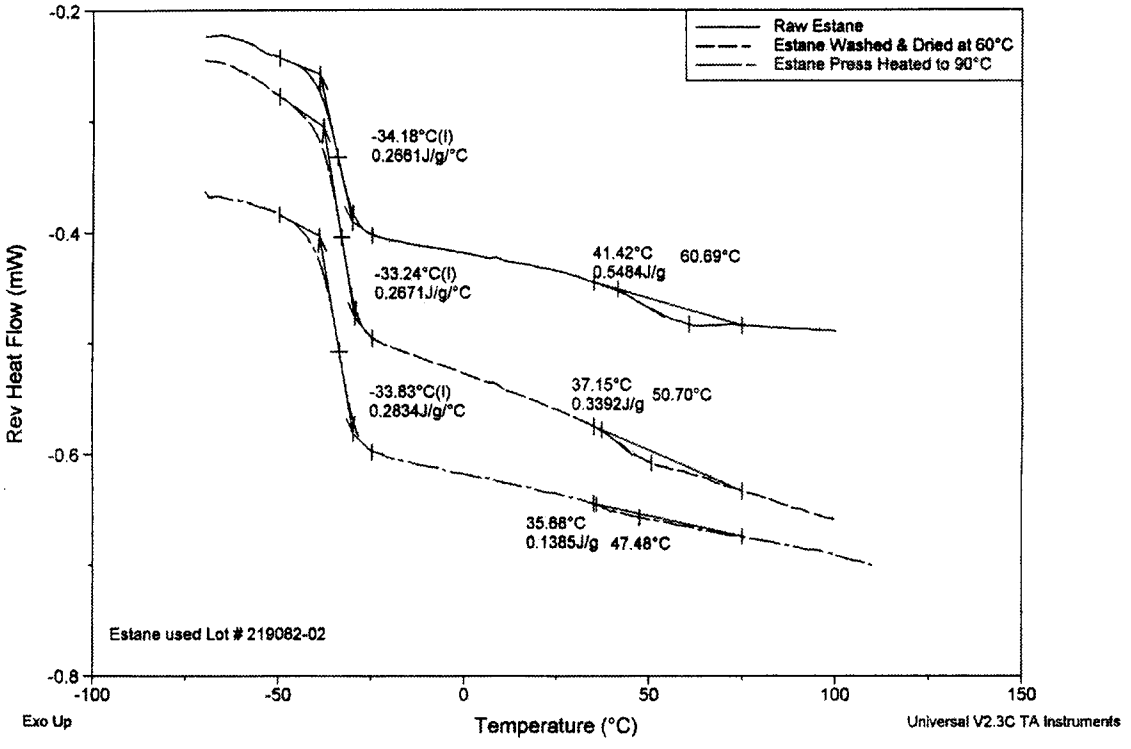

Fig. 2. Heat and pressure affect the T_g and softening temperature of Estane.

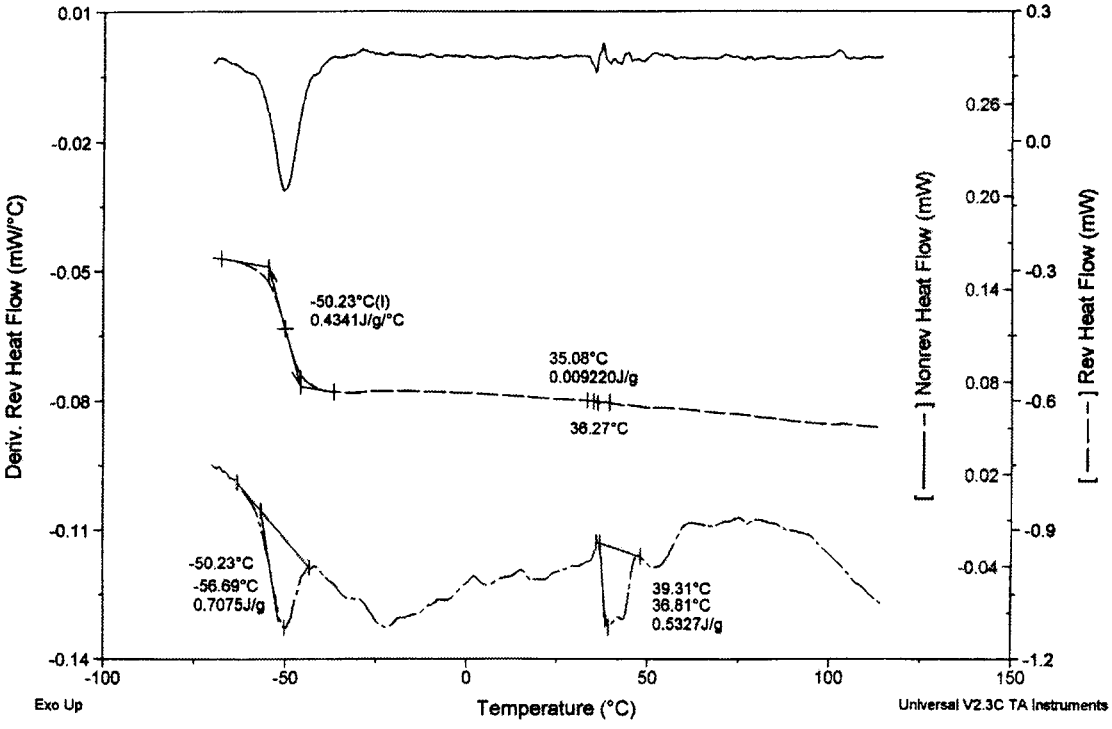

Fig. 3. M-DSC analysis of the binder of PBX 9501 shows the reversible, its derivative, and nonreversible thermal transitions.

T_g of the PBX. The T_g did not change after pressing at 90°C and 30 kpsi, but a second run on the same sample one day after heating to 120°C showed a higher T_g at −46.8°C (Fig. 4).

Pressed PBX 9501 aged for 16.7 years under inert atmosphere near ambient temperature was machined into chips and tested for change in T_g. Fig. 4 also compares the aged T_g data with its original molding powder and a recently pressed sample from the molding powder. It appears that the aged is very similar to the thermally relaxed pressed sample.

3.4. Kel F 800

Kel F has a T_g close to 28°C. It has a melting endothermic transition with onset at 91°C and maximum at 98°C. Hot pressing did not change the T_g, but the softening endothermic transition began gradually at 67°C with maximum at 84°C. The change in heat capacity of the T_g was greater in the sample subjected to heat and pressure indicating a larger fraction of amorphous phase and hence a loss of crystallinity. After the pressed piece was allowed to sit at ambient temperature for 12 days, an additional measurement showed very little change. The reversible scans are shown in Fig. 5.

3.5. PBX 9502

PBX 9502 is 95 wt.% TATB and 5 wt.% Kel F as binder. Pressed and machined samples were obtained from two virgin lots (890-019 and 890-022) and one recycled lot (891-005) of PBX 9502. The T_g of PBX 9502 molding powder is 25°C, which is slightly lower than the T_g of Kel F at 28°C indicating minimal interaction between the TATB and binder. Samples pressed and aged had no change in the T_g. The pressed samples containing all virgin PBX 9502 had T_g of 25.0°C with 95% confidence limits of 1.0°C from 12 runs on two lots of molding powder. On the other hand, pressed samples with recycled PBX 9502 had T_g of 27.2°C with 95% confidence limits of 0.50°C for 7 runs. A small amount of cross-linking that could occur during pressing and machining of the

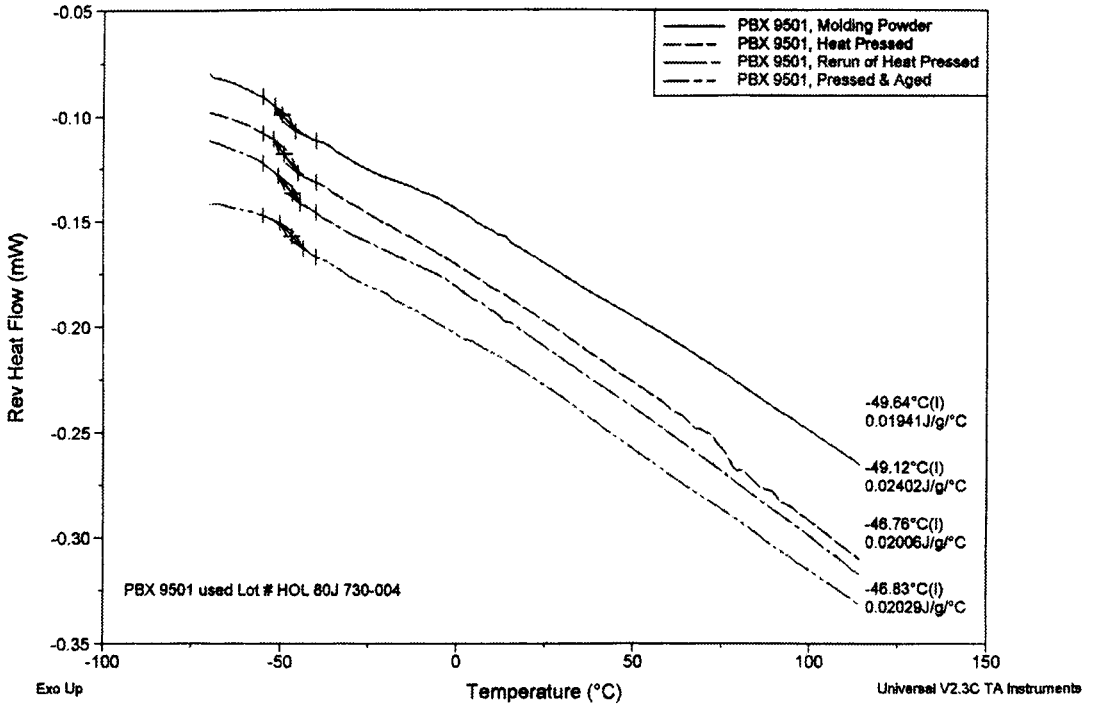

Fig. 4. A comparison of the soft segment T_g of PBX 9501 after pressing and aging.

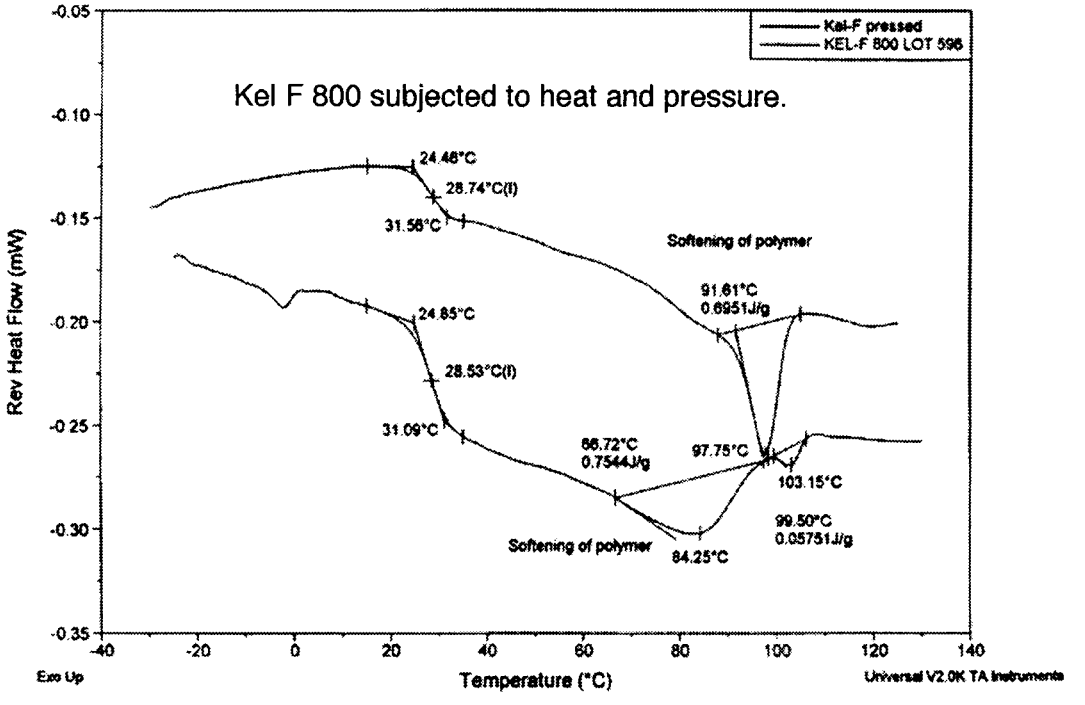

Fig. 5. Hot pressing Kel F 800 affects its thermal properties. Top scan in before and bottom scan is after heating and pressing.

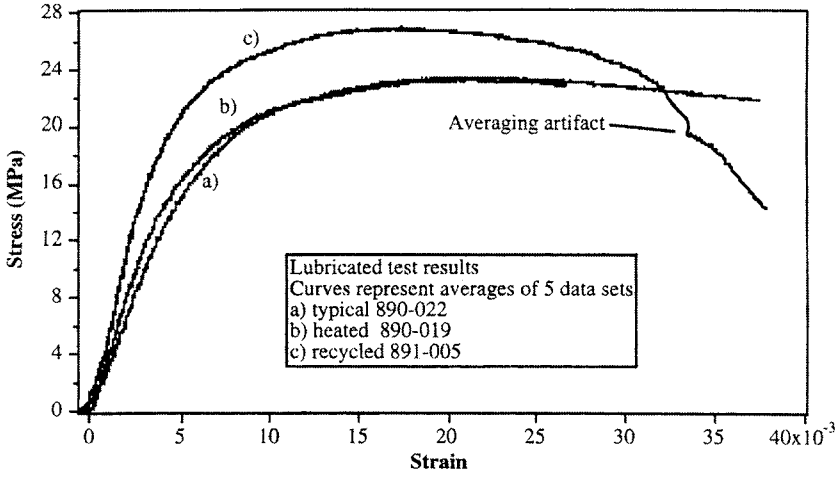

Fig. 6. Stress/strain curves comparing nominal PBX 9502 with recycled PBX 9502.

Kel F, which was recycled, might have caused an increase in the T_g.

3.6. Mechanical properties of PBX 9502

Ultimate compressive strength, strain, and elastic moduli data from virgin and recycled PBX 9502 samples show that the recycled PBX 9502 lot displays a stronger compressive strength, has a slightly higher elastic modulus, and behaves less plastically before failing than either virgin lot tested for comparison (Fig. 6) [5].

4. Conclusions

The data suggest that the glass transition temperatures of the polymers, Estane 5703 and Kel F 800 are affected slightly by the mixing with plasticizer and high explosives. The results also show that pressing does not change the soft segment glass transition temperature but appears to have an effect on the hard segment glass transition and the crystallinity of the polymer. Repeated processing can change the plasticity of PBX 9502. An analysis of the M-DSC results for the recycled and virgin PBX 9502 lots supports the results seen with the compressive mechanical measurements, that is, the recycled lot demonstrates less plasticity and more strength than the virgin lots under quasi-static ambient test conditions.

Acknowledgements

Wayne King performed GPC analysis of the Estanes. This work was performed under the auspices of the US Department of Energy.

References

[1] T.R. Gibbs, A. Popolato, LASL Explosives Property Data, University of California Press, Berkeley, 1980, pp. 454–457.
[2] B.F. Goodrich Co., Estane 5703 Product Data Sheets, And Goodrich, B.F., Adhesives Technology of Estane Polyurethane, B.F. Goodrich Speciality Chemicals, TSR 76-02 TF116, March 1995.
[3] H.H.G. Jellinek, T.J.Y. Wang, Reaction of NO_2 with linear polyurethane, J. Polym. Sci., Polym. Chem. Ed. 11 (1973) 3227.
[4] D.J. Idar, R.L. Rabie, P. D. Scott, Quasi-Static, Low-Strain Rate Compression Measurements of Thermally Treated and Mechanically Insulted PBX 9502 Samples, Los Alamos National Laboratory report LA-UR-97-5116, December 1997.
[5] C.B. Skidmore, D.J. Idar, G.A. Buntain, S.F. Sun, R.K. Sander, Aging and PBX 9502, Los Alamos National Laboratory report LA-UR-98-1206, Proceedings of 1998 Life Cycles of Energetic Materials, Fullerton, CA, 29 March–1 April 1998.