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Title: EFFECTS OF TEMPERATURE AND PRESSURE ON THE
GLASS TRANSITIONS OF PLASTIC BONDED EXPLOSIVES

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EFFECTS OF TEMPERATURE AND PRESSURE ON THE GLASS TRANSITIONS OF PLASTIC BONDED EXPLOSIVES

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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 will be measured for the samples.

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_g 's 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/vinylidene 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) needs 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 copolymer made from a combination of soft segments and hard segments bonded by ester and 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.

EXPERIMENTAL

Equipment

The T_g and endothermic polymeric relaxation data were obtained using the modulated option on TA Instruments Differential Scanning Calorimeter (DSC) 2920. Unlike the traditional DSC, which can not 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 and endothermic polymer relaxation is non-reversible. The DSC 2920 electronics

and software separate the total heat flow 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.

Sample Preparation:

Approximately 18-mg samples were pressed into crimped aluminum 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.

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

Data Storage: Off

Modulate at +/-1.000°C every 60 seconds

Isothermal for 4 minutes

Data Storage: On

Sampling interval 1.0 sec/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 only cooled to -30°C.

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 an aqueous 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.

Recycled PBX 9502 has 50 wt% machine turnings from the pressed billets added to the slurry of TATB before adding the additional Kel F in ethyl acetate. Additional water is added to form the molding powder.

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 11123 Materials Testing Workstation with 6.0-in. diam compression anvils, a 5000 lb_f maximum load cell, and an extensometer gauge to measure strain. Load and extensometer voltage measurements were obtained with a LeCroy 9400A oscilloscope. Data were acquired using GPIB interface macros written in Igor Pro and loaded on a Macintosh Powerbook 170. 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

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.

RESULTS AND DISCUSSION

The glass transition of a highly filled polymer is only seen with a sensitive DSC and 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 has a larger change in heat capacity than Kel F 800 because it is less crystalline. We are able to measure the T_g change in the filled polymer on both by using the minimum of the derivative of the reversible trace in the temperature region of the T_g to confirm the T_g inflection. Melting of the soft segment and glass transition of the hard segments are in similar temperature range so again the derivative of the reversible trace was used to differentiate between melting with negative and positive inversion points and glass transition with a negative inversion.

Estane 5703

We found the glass transition of some older samples of Estane had shifted to a lower temperature. 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 hydrolyzes 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 . Figure 1 compares the T_g with the Mw data for samples.

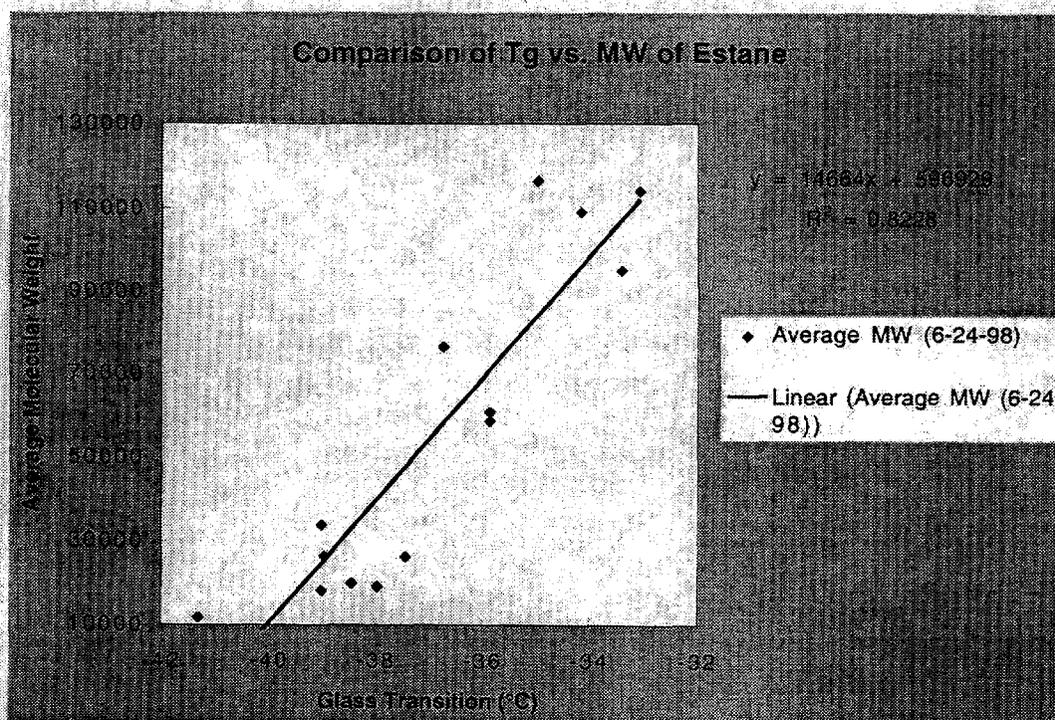


Fig. 1. Aged Estane with a lower Mw has a lower T_g .

The sample used for the pressing study had been exposed to ambient conditions for a few months and had a Mw of 111,000. The T_g of the soft segments was not affected by heating to 90 °C and pressing, but the heat of softening is much less on the pressed sample and even less on the heated sample, which was tested several months afterward, Fig 2.

PBX 9501 Binder

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. Figure 3 shows the M-DSC thermal analysis for the binder. The nonreversible trace shows an endothermic relaxation of the binder with very little reversible melting at 35°C.

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 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 . Figure 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. We plan to test samples that have been in an abnormal environment as well.

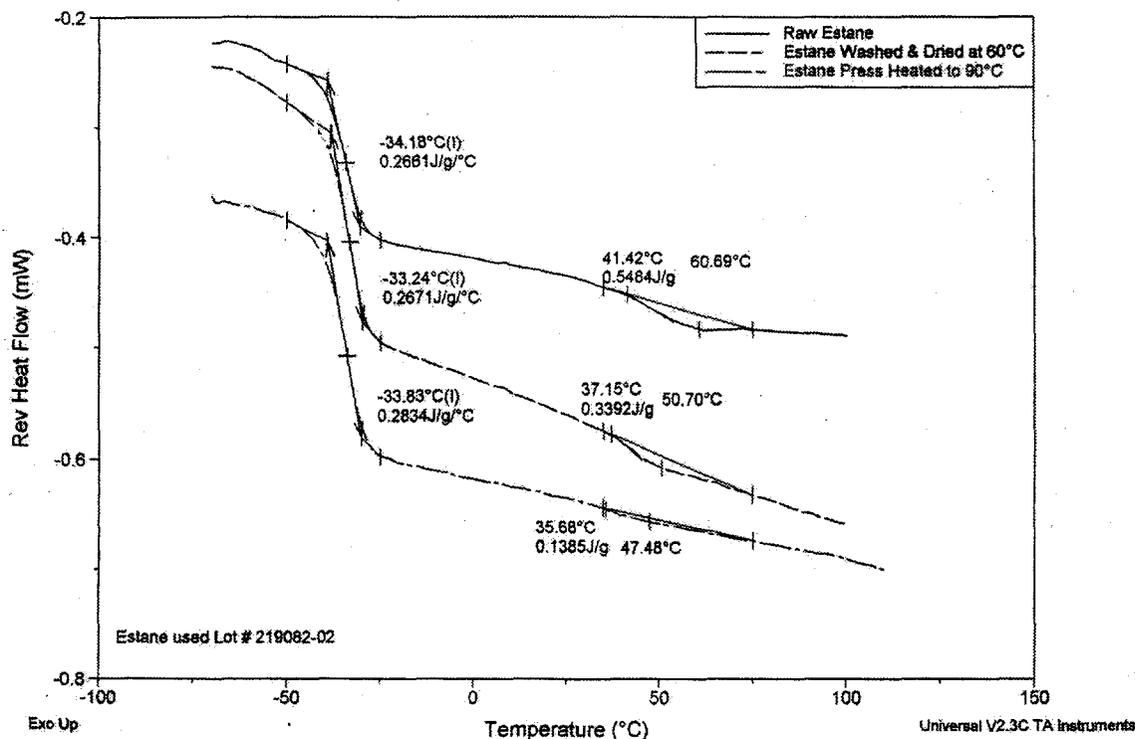


Fig. 2. Heat and pressure affect the T_g and softening temperature of Estane.

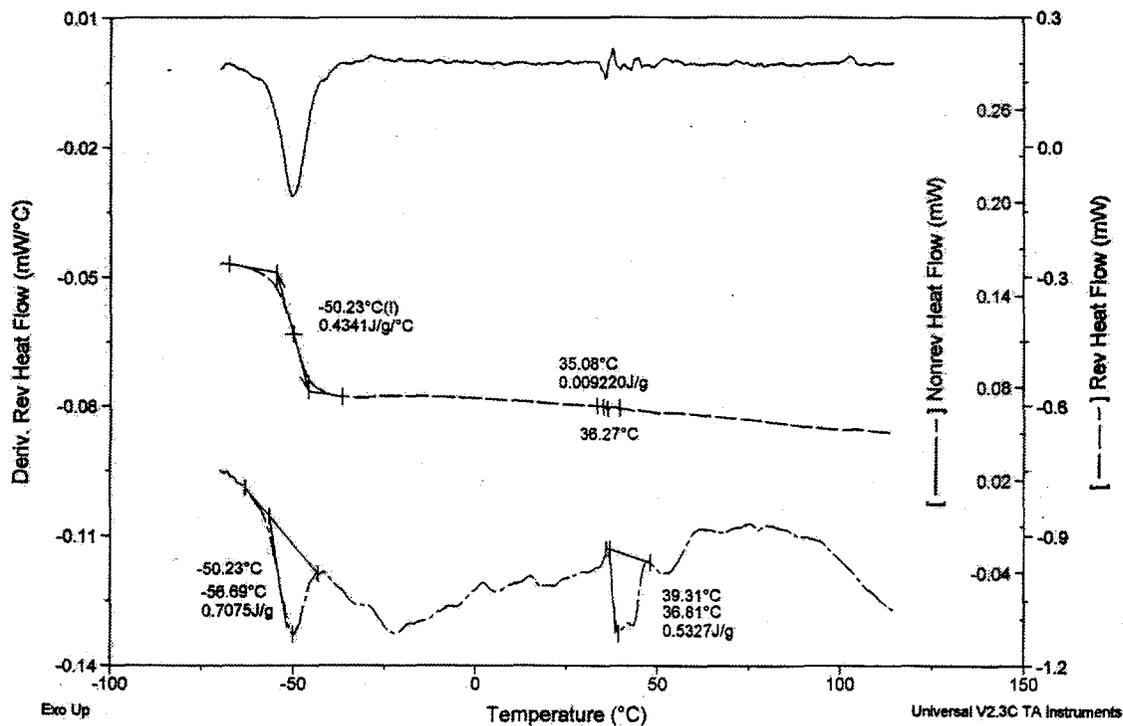


Fig. 3. M-DSC analysis of the binder of PBX 9501 shows the reversible, its derivative and nonreversible thermal transitions.

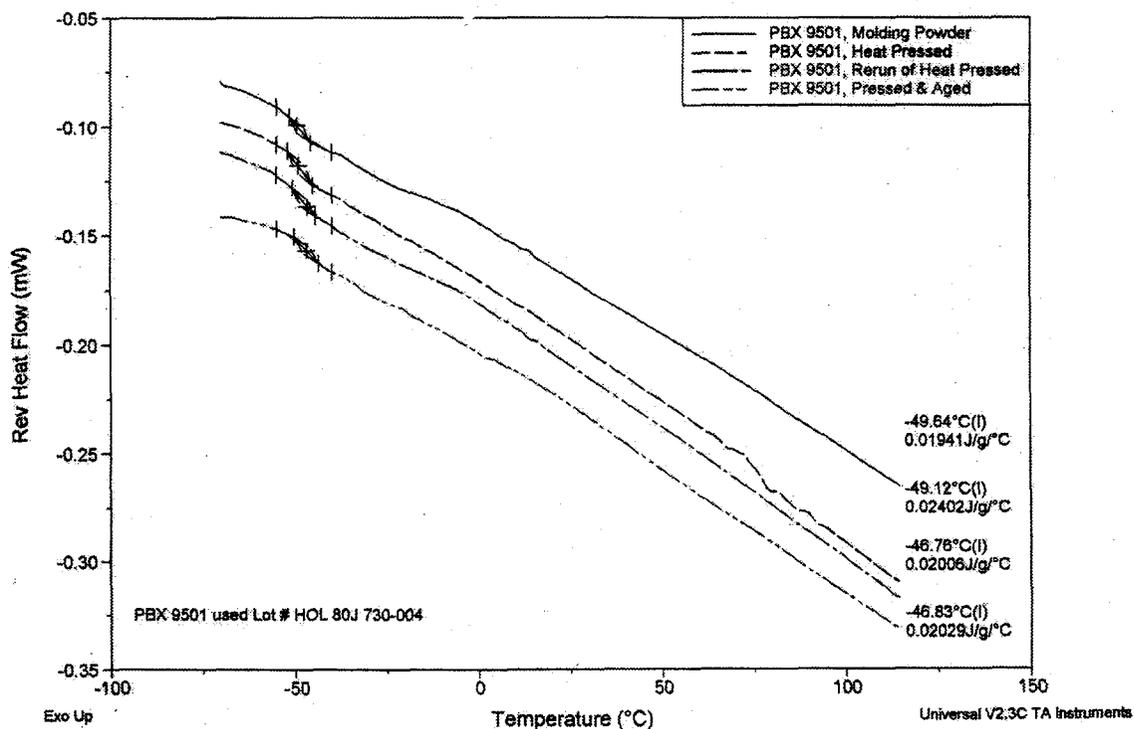


Fig. 4. A comparison of the soft segment T_g of PBX 9501 after pressing and aging.

Kel-F 800

Kel F has a T_g close to 28 C. Hot pressing did not change the T_g , but softening temperature was much less sharp and the change in heat capacity of the T_g was greater indicating 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.

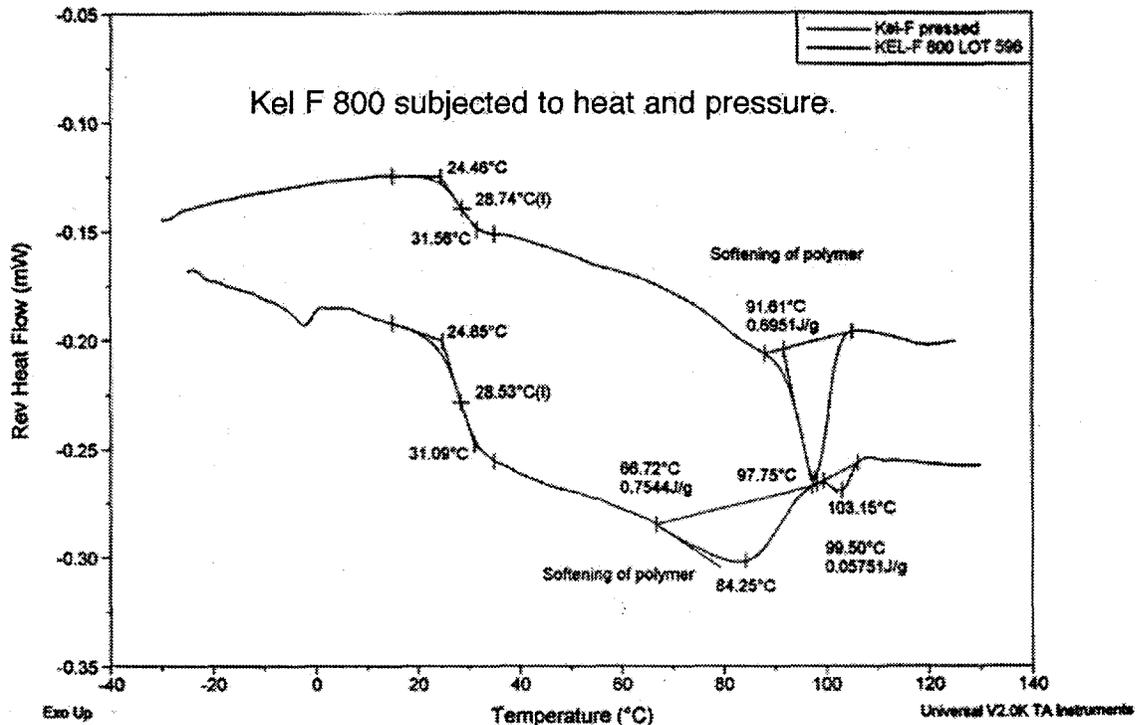


Fig. 5. Hot pressing Kel F 800 affects its thermal properties.

PBX 9502

PBX 9502 is 95-wt% TATB and 5-wt% Kel F as binder. The T_g of PBX 9502 molding powder is 25 °C 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 . Pressed samples that contained recycled PBX 9502 had a T_g of 27.1 with 95% confidence variation of 0.5%. The original molding powder was T_g of 25.1°C and a pressed sample containing all new PBX 9502 had T_g of 25.0 °C with 95% confidence limits of 1.02 °C from twelve runs with two lots of molding powder. On the other hand, pressed samples with recycled PBX 9502 had T_g of 27.2 °C with 0.50% confidence limits for 7 runs. An increase in cross-linking due to the additional processing may have caused the increase in the T_g .

Mechanical Properties of PBX 9502

Compressive strength and elastic modulus data from samples made from 50-wt% recycled PBX 9502 show that it exhibits greater compressive strength, a higher elastic modulus, and behaves less plastically before failing than either nominal lot, Fig.6.⁵

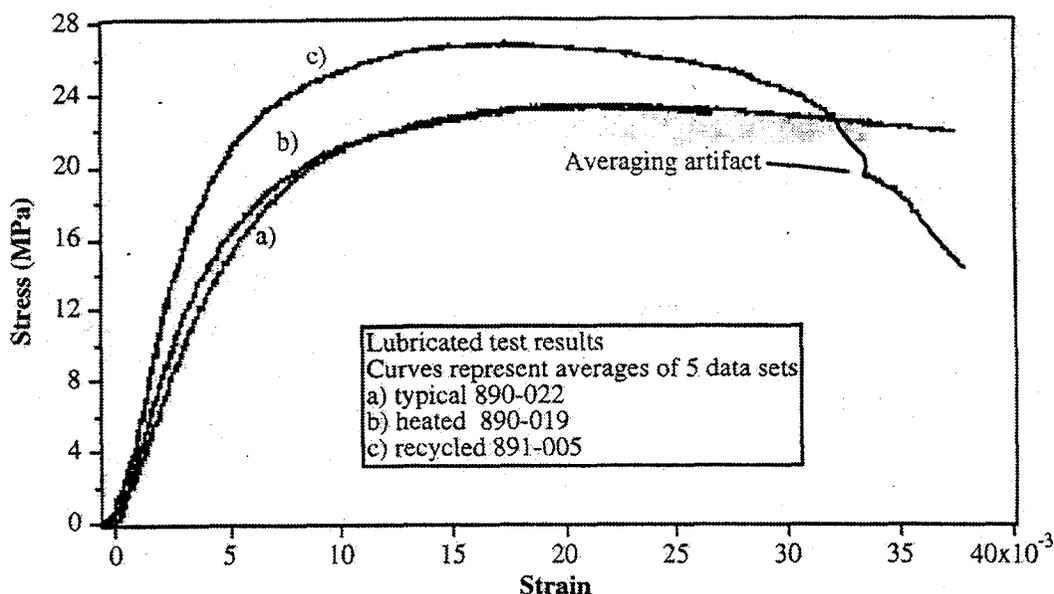


Fig. 6. Stress/strain curves comparing nominal PBX 9502 with recycled PBX 9502.

CONCLUSIONS

Hot pressing does not change the soft segment glass transition 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 the PBX. After Estane degrades to a lower M_w its T_g decreases. Additional studies may give more insight into the behavior of the binder under different conditions.

ACKNOWLEDGMENTS

Wayne King performed GPC analysis of the Estanes and Matthew Holmes measured the compression of the PBX 9502 lots.

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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 and T. J. Y. Wang, "Reaction of NO_2 with Linear Polyurethane," *J. Polym. Science, Polym. Chem. Ed.*, **11**, 3227 (1973).
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Los Alamos National Laboratory

1998 NATAS Conference

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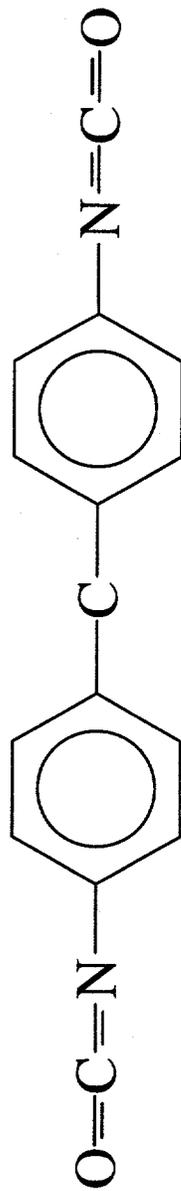
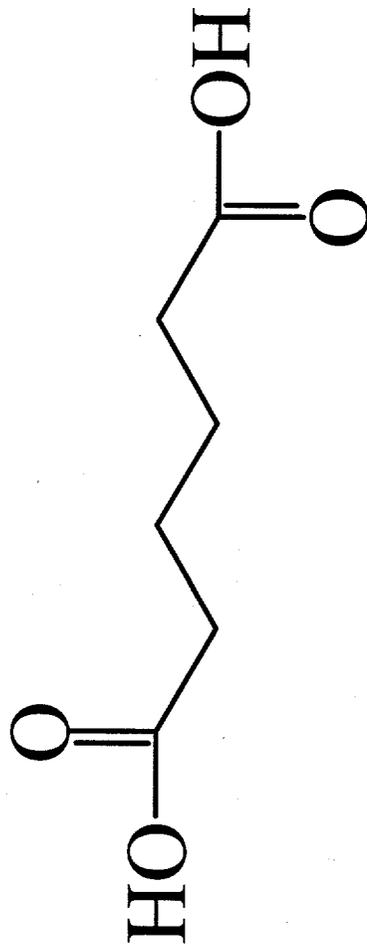
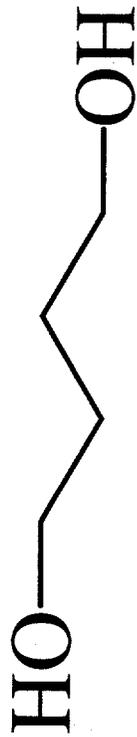
High Explosives Science & Technology

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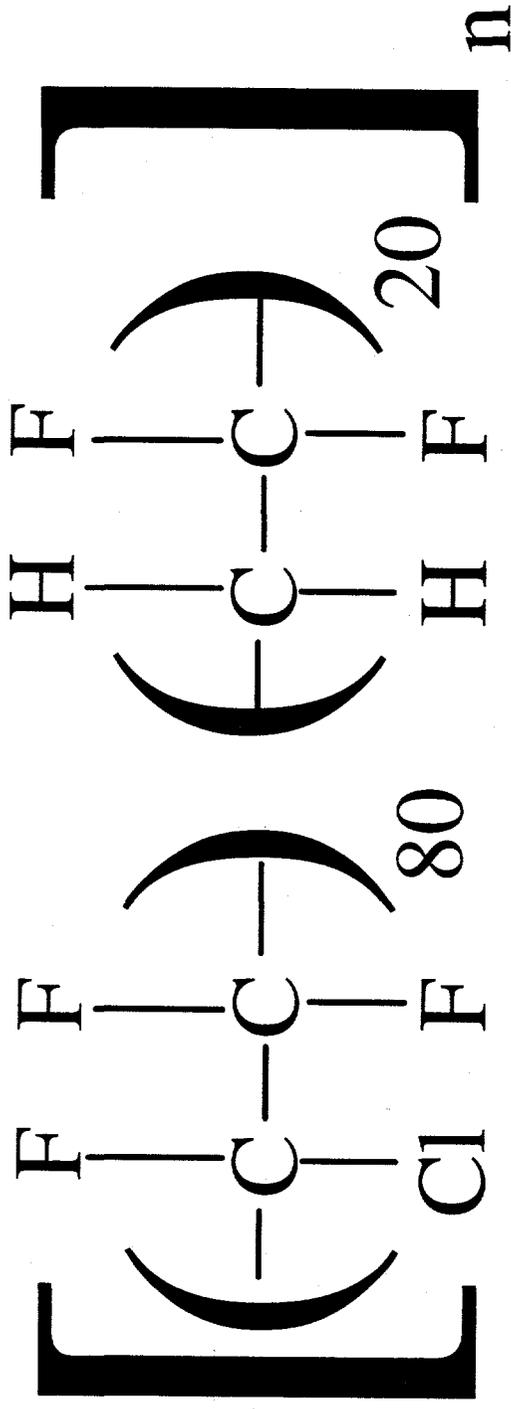
Outline

- **Plastic bonded explosives**
- **Experimental**
- **Aging of Estane vs Glass Transition Temperature**
- **Estane changes with Heat Pressing**
- **Plasticizer effects on Estane**
- **Kel F 800 changes with Heat Pressing**
- **Processing changes to mechanical properties**

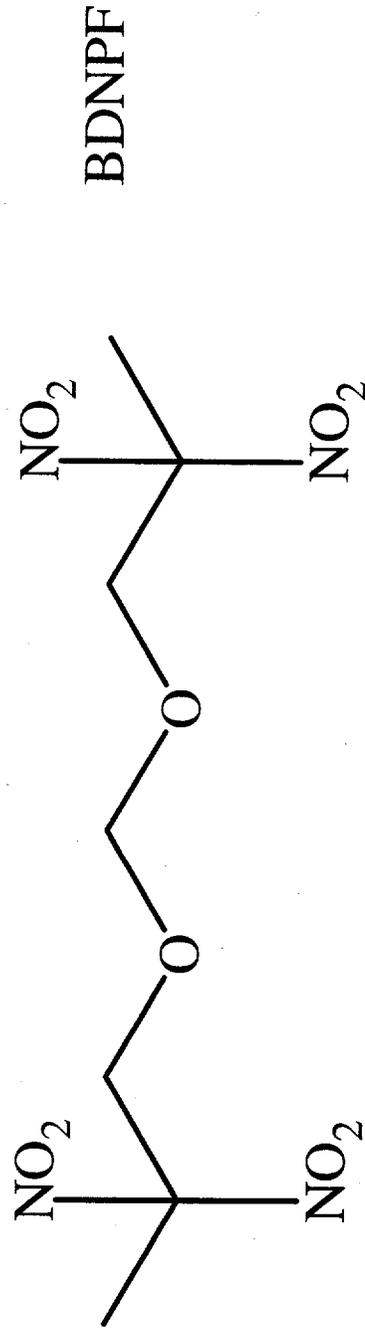
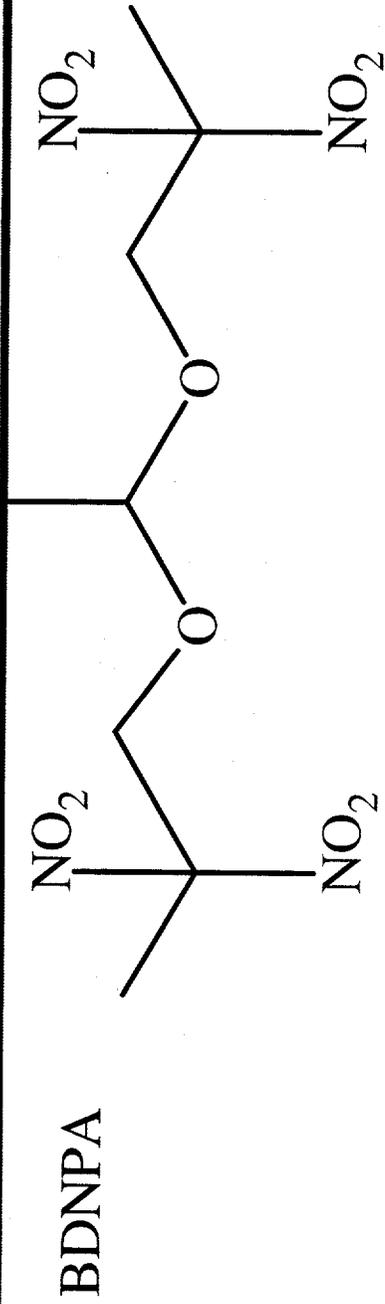
Estane Components



Molecular Structure of Kel-F 800



NITROPLASTICIZER



Composition of PBXs

- PBX 9501 is 95 wt% HMX, 2.5 wt% Estane and 2.5 wt% nitroplasticizer
- PBX 9502 is 95 wt% TATB and 5 wt% KeI F 800

Materials Processing Methods

- Estane from B. F. Goodrich and Kel F from 3M
- Binder from dissolving Estane and nitroplasticizer in acetone, casting, and drying
- PBX by slurry method: binder in solvent added to HE slurried in water and solvent removed to form binder covered HE molding powder.
- Cylindrical samples heat pressed at 90°C at 30 kpsi
- Recycled PBX 9502 is a 50/50 mixture of reslurried previously pressed machine turnings with new TATB and additional Kel F lacquer.

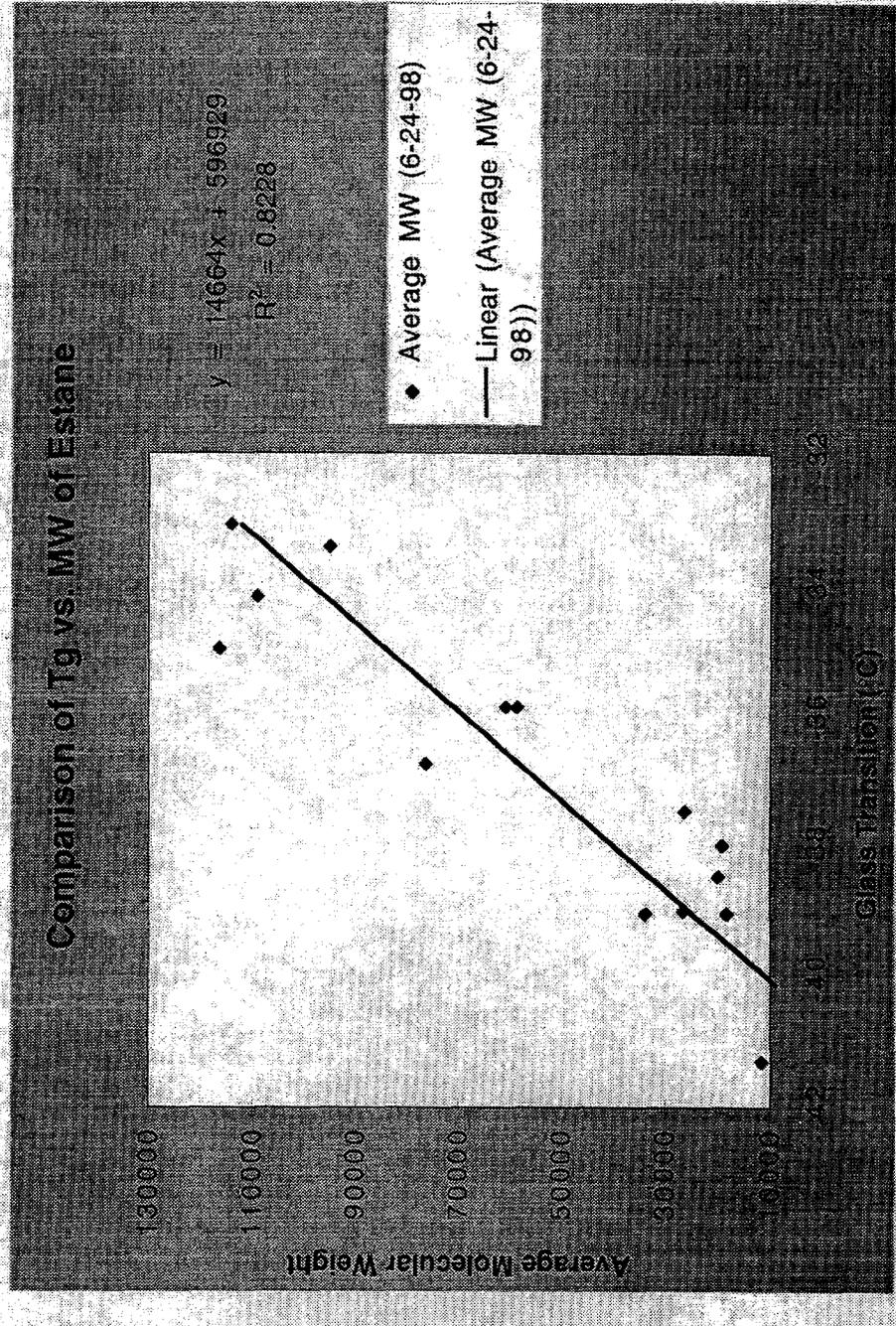
Thermal Experimental Method

- 18-mg sample and glass bead reference in crimped Al pans within 0.5 mg equal weight
- Equilibrate at -74°C for Estane or -30°C for Kel F
- Modulated at $\pm 1.0^{\circ}\text{C}$ with 60 s period
- Ramp at $2^{\circ}\text{C}/\text{min}$ to 120°C
- Data Storage off
- Equilibrate at 50°C

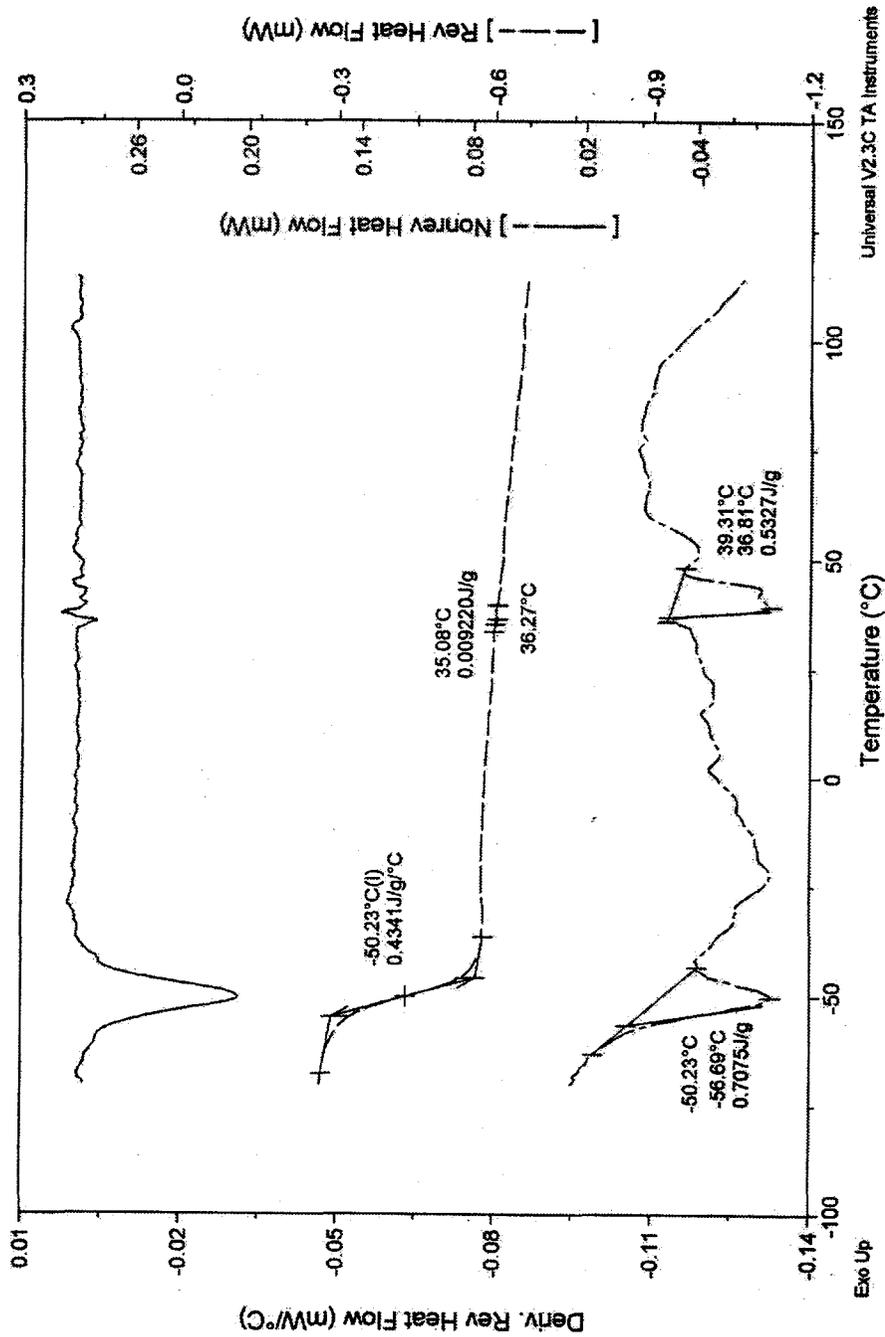
Analysis

- Gel permeation chromatography run on Water GPC with THF solution of Estane.
- Average molecular weight found by comparison of retention time of polystyrene standards.
- Compression Tests run on Instron 11123 Materials Testing Workstation with 5000-lb load range with strain rate of 0.0083 s⁻¹

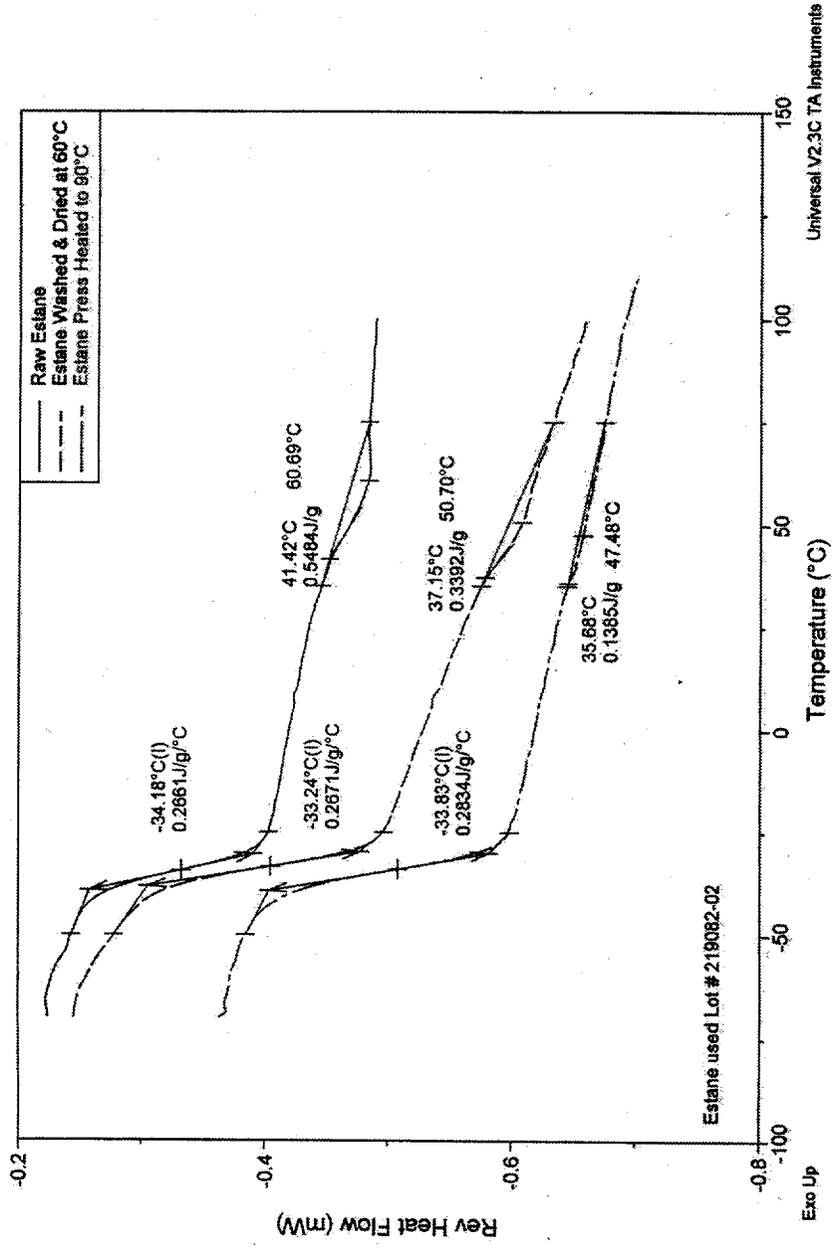
Relation of Glass Transition Temperature to Average Molecular Weight of Aged Estane



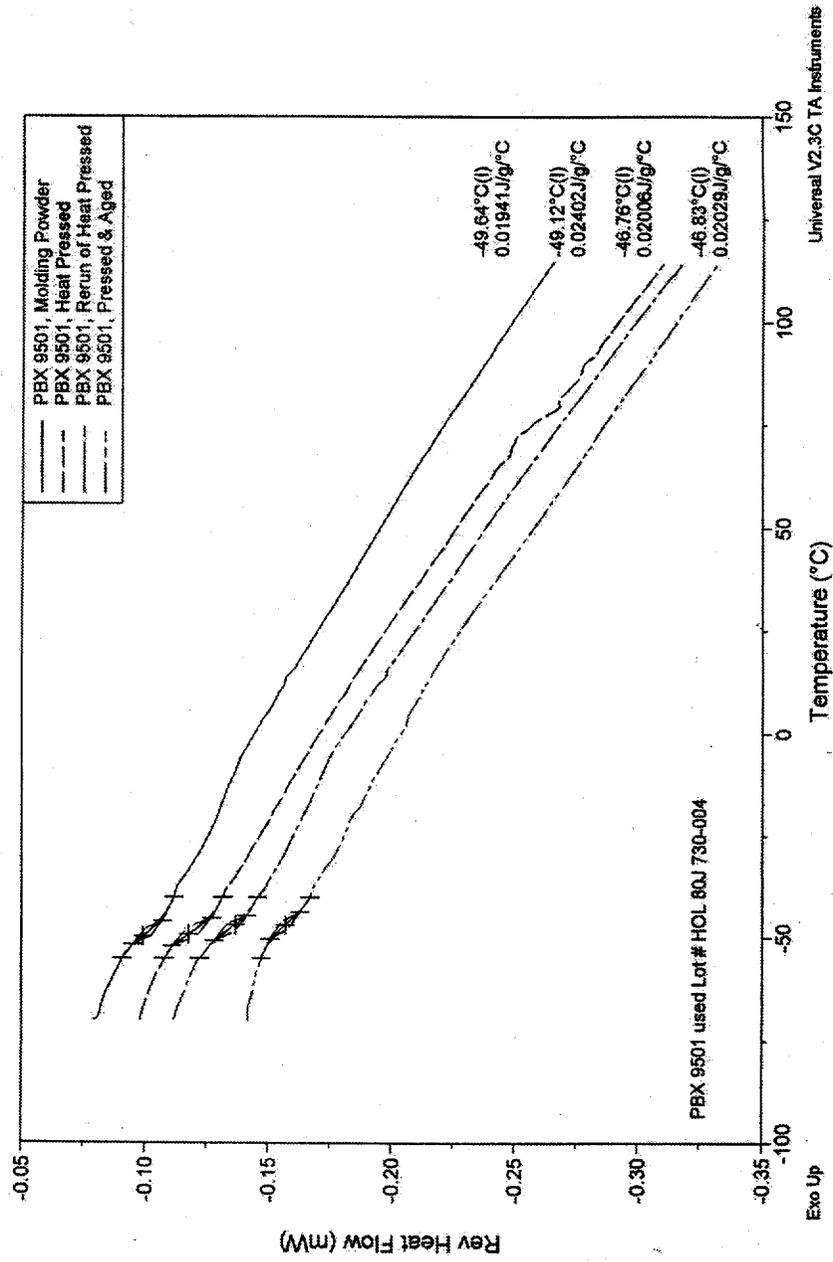
M-DSC of Binder



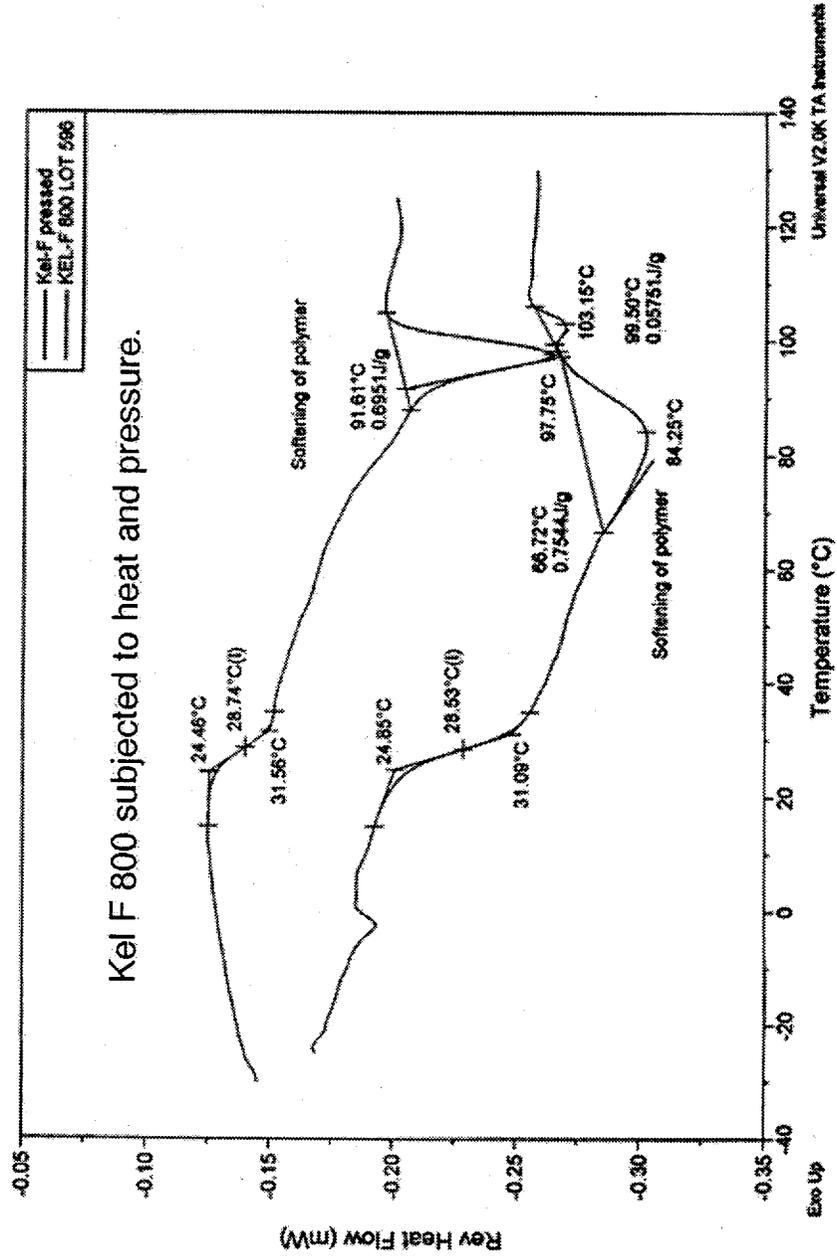
Heat Pressing Effect on Estane



Heat Pressing Effect on PBX 9501



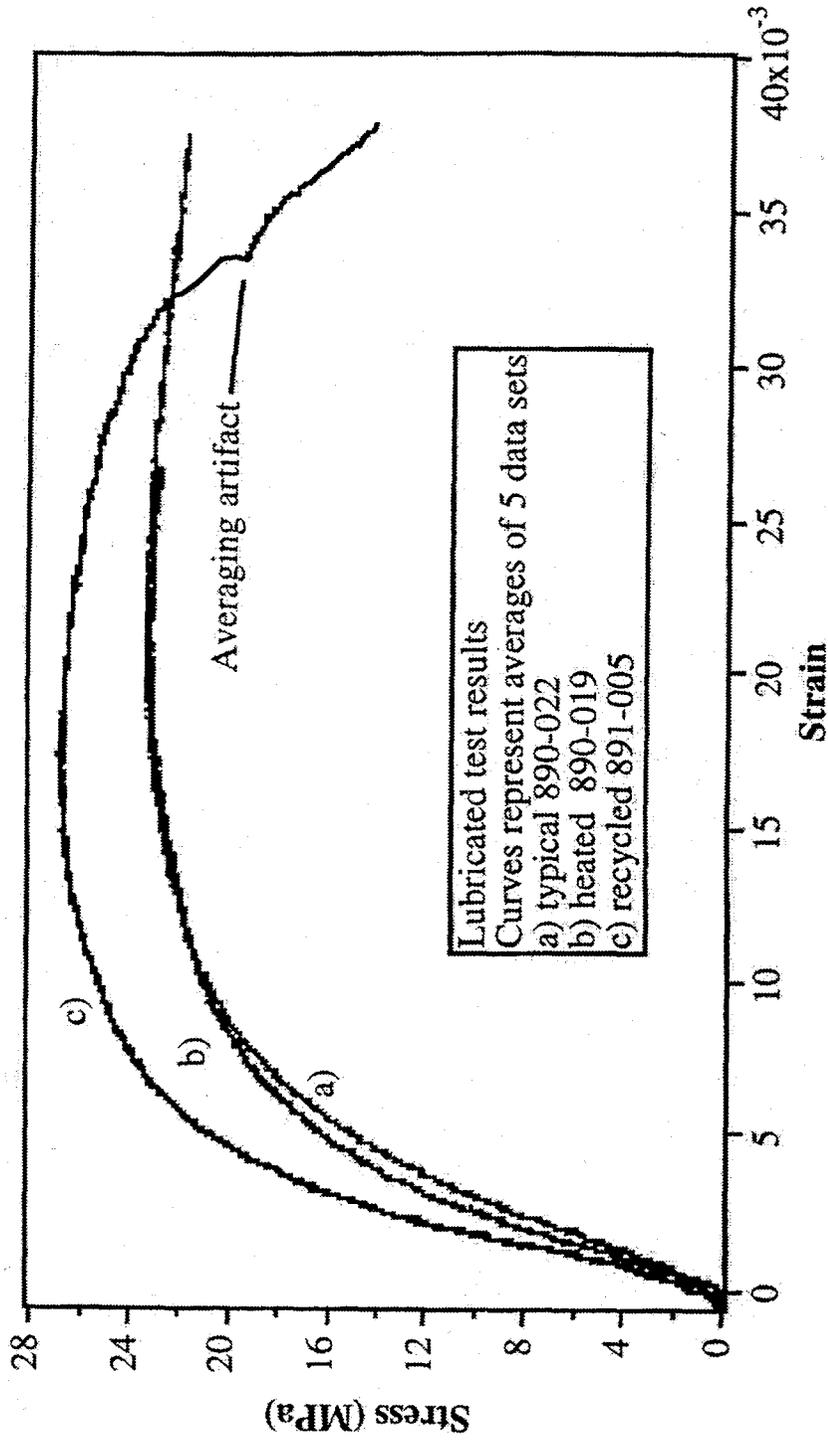
Heat Pressing Effect on Kel F 800



The Difference of T_g of Kel F in Recycled PBX 9502

Sample	T_g ($^{\circ}\text{C}$)	95% Conf. ($^{\circ}\text{C}$)
Molding Powder	25	1
Pressed Molding Powder	25.0	1.0
Pressed Recycled	27.2	0.5

Comparison of Recycled and Virgin PBX 9502 Stress/Strain Curves



Conclusions and Future Studies

- Hot pressing does not change the soft segment T_g but affects the crystallinity.
- Recycled PBX 9502 is stiffer and begins to fail at a lower strain rate.
- As Estane degrades to a lower M_w its T_g decreases.
- Further experiments with different pressures and temperatures to be done.