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Dynamic Mechanical and Molecular Weight Measurements on Polymer Bonded Explosives from Thermally Accelerated Aging Tests
II. A Poly(ester-urethane) Binder

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Dynamic Mechanical and Molecular Weight Measurements on Polymer Bonded Explosives from Thermally Accelerated Aging Tests II. A Poly(ester-urethane) Binder.*

by

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ABSTRACT

The molecular weight distribution and dynamic mechanical properties of an experimental polymer bonded explosive, X-0282, maintained at 23, 60, and 74°C for 3.75 years were examined, X-0282 is 95.5% 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclo-octane explosive and 4.5% Estane 5703, a segmented poly(ester-urethane).

Two mechanical relaxations at about -24 and 42°C were found in the X-0282 aged at room temperature for 3.75 years. A third relaxation at about 85°C was found in X-0282 aged at 60 and 74°C. The relaxation at -24°C is associated with the soft segment glass transition of the binder. The relaxation at 42°C is associated with the soft segment melting and may also contain a component due to the hard segment glass transition. The relaxation at 85°C is probably associated with improved soft segment crystallite perfection. The molecular weight of the poly(ester-urethane) binder decreased significantly with increasing accelerated aging temperature. A simple random chain scission model of the urethane degradation kinetics in the presence of explosive yields an activation energy of 11.6 kcal/mole. This model predicts a use life of about 17.5 years under the worst military operating conditions (continuous operation at 74°C).

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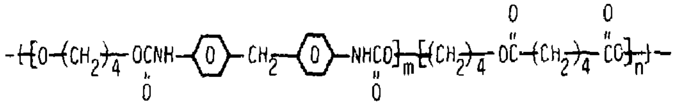
INTRODUCTION

Although fluoropolymers have exceptional thermal stability as binders for explosives, they do not desensitize HMX explosives. Humphrey[1] found that Estane 5702-F1, a B. F. Goodrich poly(ester-urethane) had improved insensitivity over fluoroelastomers and plasticized nitrocellulose binders. The question we attempt to answer is whether or not this reduced sensitivity PBX can withstand the 20 year stockpile life required for current military explosives.

The dynamic mechanical properties and molecular weight distribution of X-0282, an experimental polymer bonded explosive (PBX), maintained at 23, 60, and 74°C for 3.75 years were examined. Because of a relaxation in the Estane 5703, a poly(ester-urethane) binder similar to Estane 5702-F1, at 42°C associated with soft segment melting and/or the hard segment glass transition, mechanism changes above and below this transition cannot be ignored. Surprisingly, the decrease in molecular weight with accelerating aging temperature obeys the random chain scission model reasonably well yielding an activation energy of 11.6 kcal/mole. The model predicts a use-life of about 17.5 years under the worst possible military conditions (74°C). A considerably longer use-life is predicted for less stringent conditions.

EXPERIMENTAL

The molecular weight distribution and dynamic mechanical properties of X-0282 maintained at 23, 60, 74°C for 3.75 years were studied using a Waters model 100 GPC and a Rheometrics mechanical spectrometer. X-0282 is composed of 95.5 weight percent 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) and 4.5 weight percent Estane 5703, a segmented poly(ester-urethane) manufactured by B. F. Goodrich Co. Estane 5703 is a segmented polyurethane[2] of low molecular weight poly(butylene adipate) soft segments and 4,4'diphenylmethanediisocyanate-1,4-butanediol hard segments. The resulting polyurethane repeat unit is approximately



where the number of butylene adipate repeat units (n) in the soft segment is 4-6 and the average number of urethane repeat units (m) in the hard segment is 1-3.

In the DSC trace in Fig. 1, the soft segment T_g occurs at -28°C and a broad melting endotherm associated with soft segment melting is observed between 40 and 80°C. From our previous work,[3] the hard segment glass transition should fall in this region, but is obscured by the soft segment melting endotherm. The hard segment melting occurs at about 130°C[4] which is outside the military range.

RESULTS

Dynamic Mechanical Properties of X-0282. The complex molecular architecture and low concentration of the poly(ester-urethane) binder in the PBX makes interpretation of the dynamic mechanical properties of the aged PBXs extremely complex. The shear storage modulus (G') and tangent delta are plotted as functions of temperature in Fig. 2 for X-0282 aged at 23, 60 and 74°C for 3.75 years. The room temperature aged PBX has only two relaxations at -23 and 41°C for the 1 Hz. measurement. These are associated with the soft segment T_g and melting found in the DSC trace in Fig. 1. The PBXs aged at 60 and 74°C exhibit a third relaxation at about 70°C which is most intense in the sample aged at 60°C.

Since the soft segments melt between 40 and 80°C, isothermal aging in this range would be equivalent to annealing. Annealing improves the perfection of the higher molecular weight soft segment chains, but some fraction of the lower molecular weight chains will remain molten. The amount of molten soft segments will increase at higher annealing temperatures. As a result, aging at supercoolings of 15-25°C below the melting point of the most perfect soft segment crystals will produce many crystallites of moderate perfection. The 60°C aged X-0282 has a large concentration of cyrstallites of moderate perfection which are responsible for the strong relaxation at 65°C and some low molecular weight soft segments which crystallize on cooling to produce the soft segment relaxation at 42°C. Aging or annealing X-0282 at 74°C would produce fewer crystallites of higher perfection than at 60°C and a higher concentration of molten soft segment during the accelerated aging test. Thus the 74°C aged X-0282 shows a weaker relaxation due to the lower concentration of soft segment crystallites at a higher temperature (80°C) because of their perfection. The higher concentration of molten soft segments succeptable to the ester interchange degradation reaction in the 74°C aged X-0282 may explain the lower melting point of the low molecular weight soft segment component (30°C) found in this sample.

In the 23°C accelerated aging test the crystallinity of the soft segments does not improve, which explains the absence of the third relaxation. The relaxations are listed as $T_g(SS)$ for the glass transition temperature of the soft segments, $T_m(SS)$ for the low molecular weight soft segment component melting transition, and $T_A(SS)$ for the melting transition of the annealed soft segments in Table 1. The shear storage modulus at -54, 23, and 74°C is also given in the table.

Table 1. Transitions and moduli of thermally accelerated aging test samples of X-0282.

Transition	23°C/3.75 yrs	60°C/3.75 yrs	74°C/3.75 yrs
$T_g(SS)$°C	-23	-24	-24
$E_{ACT}(SS)$ kcal/mole	84	79	[illegible]
$T_m(SS)$°C	41	42	[illegible]
$T_A(SS)$°C	-	65	80
Modulus			
$G'(-54°C)\times10^{-9}$Pa	3.28	3.27	[illegible]
$G'(23°C)\times10^{-9}$Pa	1.30	1.70	[illegible]
$G'(74°C)\times10^{-9}$Pa	0.31	0.50	[illegible]

In previous work[3] MDI-butanediol polyurethane hard segments melted between 80 and 90°C depending on hard segment concentration, solubility in the soft segment, and thermal history. At higher hard segment concentrations hard segment melting occurs between 110 and 175°C.[4] Therefore, the third relaxation in X-0282 at the higher accelerated aging temperatures is not related to hard segment melting.

Molecular Weight and Binder Degradation in X-0282. Because of the poly(ester-urethane) ester linkages in both hard and soft segments in this PBX binder, ester interchange could occur in both segments. However, the rate of interchange should be most rapid in the soft segments[5,6] because of their lower bond energy and their being above T_g(SS). In the presence of the HMX explosive, the molecular weight of the segmented poly(ester-urethane) decreased with increasing accelerated aging temperature as shown in Table II. Since there are multiple segments per chain and the polydispersity remains constant at about 2.1, deterioration of the difunctional ester groups in the soft segments along the polymer backbone is assumed to be random enough for the random chain scission model to apply.

Using Eq. 2 from the previous paper to obtain the pseudo-first order rate constants k, then plotting ln k versus inverse accelerated aging temperature yields Fig. 3. According to Eq. 3 from the preceeding paper, the activation energy of the overall degradation process is 11.6 kcal/mole and the frequency factor is 2.1 x 10^2 g/mole-yr. This result is lower than that found for similar poly(ester-urethanes) in high humidity studies,[5] but not inconsistant with activation energies of other uncatalyzed linear aliphatic ester interchange reactions.[7]

Since the temperature excursion seen in military operations is from -54 to 74°C, the use-life of the poly(ester-urethane) under the worst military conditions would be only 17.5 years assuming a critical molecular weight of 5000. Obviously, in no military application will the PBX see continuous use at 74°C for 20 years, and therefore depending on the actual use temperature cycle increased use-life may be expected. Furthermore, safety considerations may preempt use-life requirements, and the insensitivity of poly(ester-urethane) binders for HMX is exceptional.[1]

Table II. Effect of thermally accelerated aging on the molecular weight of Estane-5703 in X-0282.

Aging Conditions	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
23°C/3.75 yrs	7.16 ± 0.05	15.5 ± 0.1	2.2
60°C/3.75 yrs	3.64 ± 0.04	8.3 ± 0.1	2.3
74°C/3.75 yrs	1.90 ± 0.02	2.87 ± 0.06	2.0
unaged	6.4	-	-

CONCLUSIONS

The dynamic mechanical property change which occurred in thermally accelerated aging experiments with X-0282 were caused by annealing phenomena in the poly(ester-urethane) soft segments in conjunction with chain scission at elevated temperatures. The strength and temperature of the annealing relaxation was dependent on the concentration and perfection of annealed soft segment crystals.

The decrease in molecular weight with increasing accelerated aging temperature followed simple pseudo-first order random chain scission kinetics. The rate constant for the overall reaction had an Arrhenius temperature dependence with an activation energy of 11.6 kcal/mole. This result is consistent with degradation of the polyester soft segments. Apparently, the distribution of soft segments in the polymer backbone is sufficiently random to allow the application of the random scission model.

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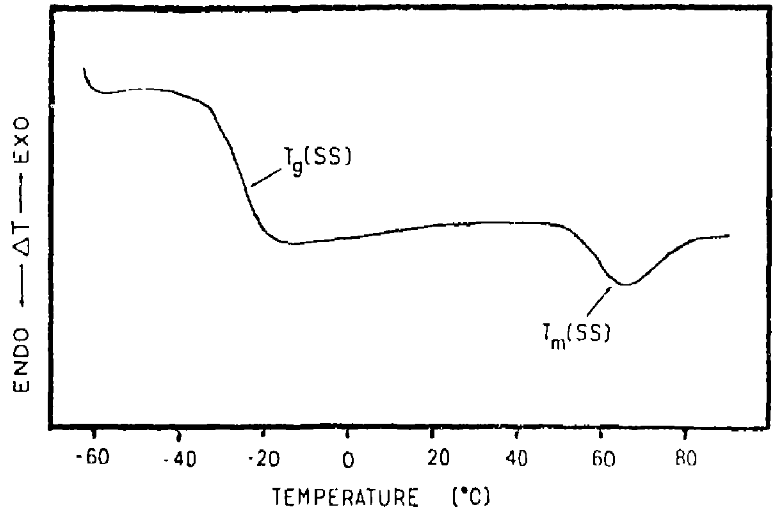

Figure 1. A DSC trace of Estane 5702-F1, a poly(ester-urethane) similar to Estane 5703, shows the soft segment glass transition, T_g(SS), at -30°C and a weak, broad melting endotherm from 45 to 80°C.

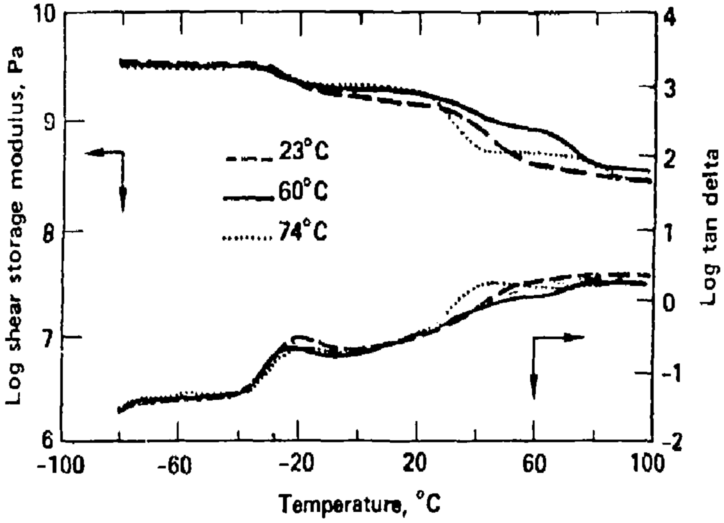

Figure 2. Shear storage modulus (G') and tan delta of X-0282 PBXs aged 3.75 years at 23, 60, and 74°C as a function of temperature at 1 Hz. show the effects of accelerated aging. The relaxation behavior caused by accelerated aging is discussed in the text.

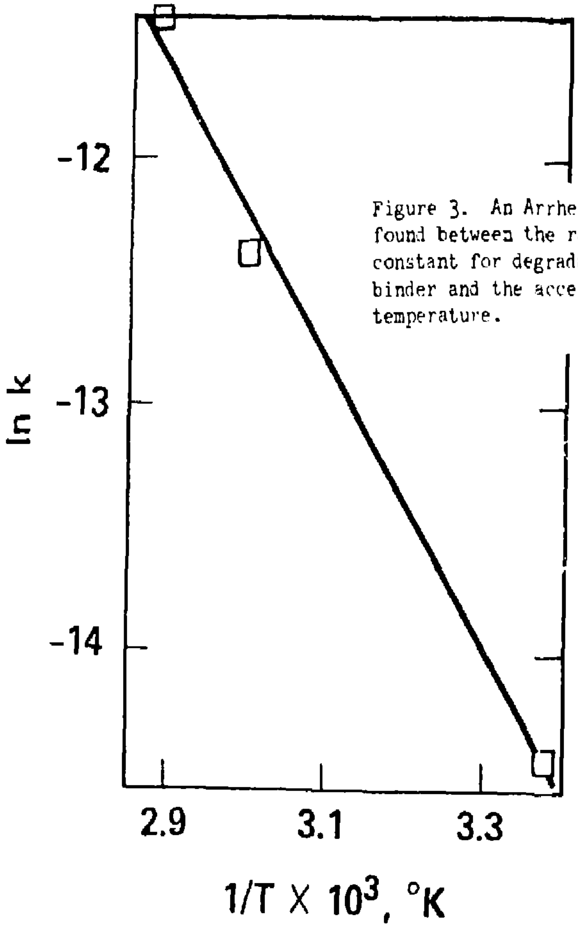

Figure 3. An Arrhenius relationship was found between the random scission rate constant for degradation of Estane 5703 binder and the accelerated aging temperature.