Dynamic Mechanical and Molecular Weight Measurements on Polymer Bonded Explosives from Thermally Accelerated Aging Tests. Kraton Block Copolymer Binder and Plasticizers

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Dynamic Mechanical and Molecular Weight Measurements on Polymer Bonded Explosives from Thermally Accelerated Aging Tests III. Kraton Block Copolymer Binder and Plasticizers.*

by

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ABSTRACT

The dynamic mechanical properties and molecular weight distribution of two experimental polymer bonded explosives, X-0287 and X-0298, maintained at 23, 60, and 74°C for 3 years were examined. X-0287 is 97% 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane explosive, 1.8% Kraton G-1650, and 1.2% B2 wax 170. X-0298 is 97.4% explosive, 1.4% Kraton G-1650, and 1.2% Cenco Hi-vac oil.

The relaxation associated with the Kraton rubber block glass transition is observed in both X-0287 and X-0298. In the unaged X-0298 it occurs at -59°C and in the aged explosive at 50°C. This is caused by migration of the oil plasticizer out of the explosive. In X-0287 the Kraton rubber block T_g is weak and broad due to the presence of the wax plasticizer. X-0287 has a second broad relaxation associated with the melting of the wax from 10 to 65°C.

The molecular weight of the Kraton binder decreased with increasing accelerated aging temperature. The oil plasticizer had no stabilizing effect, but below its melting point the wax reduced Kraton chain scission considerably. The simple random chain scission model predicted ~20.5 year use-life for X-0298, but X-0287 was stabilized against degradation below the wax melting point.

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INTRODUCTION

One of the many approaches to reducing the sensitivity of polymer bonded explosives is to add small amounts of plasticizer. The mechanisms proposed for desensitization involve modifying the heat conduction path between the external stimulus and the explosive.\textsuperscript{1,2} If semicrystalline wax is added, it can withdraw heat by melting. If oils are added, they alter the surface of the explosive and increase the loss modulus of the binder. Both processes can effectively alter the detonation behavior of the explosive.

The effect of additives on the degradation of polymers is well documented.\textsuperscript{3-5} However, oil extenders and semi-crystalline waxes are not generally used to improve polymer stability. We have analyzed the effect of Cenco Hi-Vac oil and B\textsuperscript{2} Wax 170 plasticizers on the dynamic mechanical properties and molecular weight distribution of unaged and thermally accelerated aged experimental polymer bonded explosives (PBXs) X-0298 and X-0287. The polymer binder and explosive in these PBXs were Kraton G-1650, an ABA block copolymer of styrene and hydrogenated butadiene, and 1,3,5,7-tetranitro-1,3,5,7-tetraazaacyclooctane (HMX), respectively.

The dynamic mechanical properties and molecular weight distributions of X-0287 and X-0298 experimental PBXs maintained at 23, 60, 74°C for 3 years were examined. There were no mechanical relaxations near the accelerated aging temperatures in X-0298, the Kraton/oil extended PBX. In X-0287 the wax melted over a broad range ending at about 65°C. As expected, there was a significant difference in the Kraton degradation kinetics above and below the wax melting point in X-0287. The molecular weight decrease with increasing aging temperature for the Kraton-oil system (X-0298) obeyed the random chain scission model reasonably well. An activation energy of 19.0 kcal/mole was obtained for X-0298. The model predicts a use-life of 20.5 years for both PBXs under the worst possible military conditions (74°C). A considerable improvement is predicted if operating conditions do not exceed the melting point of the wax in X-0287.
EXPERIMENTAL

The molecular weight distributions and dynamic mechanical properties of X-0287 and X-0298 maintained at 23, 60, and 74°C for 3 years were examined using a Waters model 100 GPC and a Rheometrics mechanical spectrometer. X-0287 contains 97 weight percent HMX, 1.8 weight percent Kraton G-1650, and 1.2 weight percent B\textsubscript{2}wax 170. X-0298 contains 97.4 weight percent HMX, 1.4 weight percent Kraton G-1650, and 1.2 weight percent Cenco Hi-vac oil. Kraton G-1650 is an ABA block copolymer of styrene and hydrogenated butadiene of about 15,000 and 70,000 molecular weight, respectively. Two glass transitions associated with the rubber and glassy microphases in Kraton occur at -54°C and 92°C, respectively. There is also a broad exotherm in the DSC trace of Kraton G-1650 due to crystallization and/or annealing phenomena which begins at about 20°C above the rubber block T\textsubscript{g} and ends at about room temperature. The number-average molecular weight of unaged Kraton G-1650 was 1.07 x 10\textsuperscript{5}.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties of X-0298. High vacuum oil plasticizer in Kraton G-1650 lowers the T\textsubscript{g} of the rubber block by about 12°C based on DSC results from pure Kraton (-54°C) and the oil-Kraton blend (-66°C). In the unaged PBXs the rubber block T\textsubscript{g} occurs at -59°C at 1 Hz. However, the rubber block T\textsubscript{g} in the aged PBXs occurs at -50°C ± 2°C at 1 Hz, as shown in Fig. 1 for X-0298 aged 3 years at 60°C. Further, the activation energy of this transition in the accelerated aging PBXs was 71 ± 3 kcal/mole as compared to 43 kcal/mole for unaged X-0298. This implies that during the aging period most of the oil has migrated out of the Kraton rubber block and whatever improvement in insensitivity gained by incorporation of the oil should no longer exist! Since the T\textsubscript{g}s of the rubbery Kraton block in the aged PBXs are nearly constant (50°C), oil migration is almost independent of accelerated aging temperature (see Table I). Clearly, it is undesirable for the oil to diffuse through the system and into other components.
Because of the low concentration of styrene block in the PBX, the styrene block glass transition temperature is not well resolved. Dynamic mechanical measurements on the pure block copolymer resolve the polystyrene block $T_g$ at about 97°C. This transition can be increased by up to 25°C in films cast from high solubility parameter solvents. Because of the possibility of detonating the explosive, the maximum temperature for our measurements was 120°C which may also explain the absence of a loss peak in these PBXs.

Table I lists the shear storage moduli for unaged and isothermally aged X-0298 and X-0287 experimental PBXs. Also listed are the glass transition temperatures of the rubber Kraton block and the apparent activation energies calculated from Eq. 4 in Part I. Since no major relaxations occur in the accelerated aging region, the kinetics of degradation are not expected to change.

<table>
<thead>
<tr>
<th></th>
<th>X-0298</th>
<th>X-0287</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control</td>
<td>23°C/3 yr</td>
</tr>
<tr>
<td></td>
<td>$G'(\text{-}54°C) \times 10^{-9}$Pa.</td>
<td>2.17</td>
</tr>
<tr>
<td></td>
<td>$G'(23°C) \times 10^{-9}$Pa.</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>$G'(74°C) \times 10^{-9}$Pa.</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>$T_g(G'_{\text{max}})$°C</td>
<td>-59</td>
</tr>
<tr>
<td></td>
<td>$E_{\text{Act}}$ Kcal/mole</td>
<td>47.5</td>
</tr>
</tbody>
</table>

Dynamic Mechanical Properties of X-0287. The shear storage modulus ($G'$), loss modulus ($G''$), and tangent delta for X-0287 aged 3 years at 60°C are plotted as a function of temperature at constant frequency (1 Hz.) in Fig. 2. Both the unaged and accelerated aged X-0287 PBXs contain a weak, broad relaxation from -60 to -20°C with a maximum in the loss modulus near
-40°C associated with the Kraton rubber block glass transition. From about 10 to 65°C another broad relaxation occurs that is associated with the wax melting transition.

Above the rubber block Tg, the storage modulus of X-0287 is about twice as high as that of X-0298 because of the reinforcement of the crystalline wax. As the wax melts the storage modulus of the X-0287 approaches and then drops below that of the X-0298 at about 65°C. Clearly, molten wax is a better plasticizer than the partially volatilized oil.

There is also a factor of two decrease in the loss modulus of the X-0287 compared with any aged X-0298 sample. The loss modulus of the unaged controls is quite similar above the rubber block Tg and remains nearly constant at 10^8 Pa. for both unaged PBXs until the X-0287 wax has completely melted. Since there is very little change in the loss modulus of aged and unaged X-0287, the migration of the oil plasticizer in X-0298 is responsible for the increase in loss modulus observed in aged X-0298.

Molecular weight and Polymer Degradation in X-0298 and X-0287. The molecular weight of the Kraton G-1650 decreased with increasing accelerated aging temperature for both oil extended and wax containing PBXs. The number-average molecular weights of kraton from 60°C aged X-0298 was significantly lower than 60°C aged X-0287 whereas the molecular weights from 74°C aged PBXs were almost identical (see Table 11). This implies that the wax additive successfully inhibited polymer degradation below its melting point. Indeed, applying the random scission model (Eqs. 2 and 3 from Part 1) results in an activation energy of 19 kcal/mole for the degradation of Kraton in an oil-HMX environment as opposed to 4.6 kcal/mole in an HMX-wax environment below the wax melting point (see Fig. 3). Above the wax melting point the rate constants for polymer degradation in both PBXs are nearly identical. Waxes are know to form protective coatings on hydrophobic surfaces. This protective coating would reduce the rate of attack of crosslinking and oxidizing agents on the polymer backbone. Since the wax melts at about 65°C, its ability to inhibit the diffusion of degradation promoting agents into the polymer will be reduced. Consequently, the molecular weight of the Kraton binder in X-0287 samples aged at 74°C deteriorates at the same rate as the oil extended binder.
Using the random scission model and assuming 5000 as a critical molecular weight, the use-life of the HMX/Kraton PBXs under the worst military conditions (75°C) would be about 20.5 years. Considerable improvement in this estimate occurs in the Kraton/HMX/wax system if the wax melting point is not exceeded during the aging cycle.

Table II. Effect of aging temperature on Kraton G-1650 molecular weight in X-0287 and X-0298 PBXs.

<table>
<thead>
<tr>
<th>Aging Conditions</th>
<th>$M_n \times 10^4$</th>
<th>$M_w \times 10^4$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-0287 23°C/3 yrs</td>
<td>10.37 ± 0.03</td>
<td>12.15 ± 0.03</td>
<td>1.17</td>
</tr>
<tr>
<td>60°C/3 yrs</td>
<td>9.89 ± 0.06</td>
<td>11.94 ± 0.08</td>
<td>1.21</td>
</tr>
<tr>
<td>74°C/2.3 yrs</td>
<td>2.60 ± 0.02</td>
<td>6.44 ± 0.15</td>
<td>2.30</td>
</tr>
<tr>
<td>X-0298 23°C/3 yrs</td>
<td>10.42 ± 0.03</td>
<td>12.08 ± 0.05</td>
<td>1.16</td>
</tr>
<tr>
<td>60°C/3 yrs</td>
<td>3.74 ± 0.16</td>
<td>7.90 ± 0.3</td>
<td>2.11</td>
</tr>
<tr>
<td>74°C/2.3 yrs</td>
<td>3.26 ± 0.02</td>
<td>8.60 ± 0.1</td>
<td>2.64</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Above about 65°C Kraton molecular weights degrade significantly in both X-0298 and X-0287. The oil extended binder in X-0298 follows the normal Arrhenius dependence for the random scission kinetics rate constant with inverse temperature. By comparison, the X-0287 binder degradation is identical to X-0298 at 74°C, but negligible at 60°C because the polymer is protected from oxidation by the wax. The results are consistent with dynamic mechanical observations which show the final melting of the wax at about 65°C.

Assuming that both polymer bonded explosives are equally insensitive, X-0287 has two advantages over X-0298. (1) The wax additive acts as a stabilizer against binder degradation under operating condition below its melting point. (2) Even above its melting point the wax does not migrate out of the PBX. Both PBXs just meet the 20 year use-life requirement, if they must function continuously at 74°C.
REFERENCES


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Figure 1. Shear storage ($G'$), shear loss ($G''$) moduli, and $\tan \delta$ of X-0298 aged 3 years at 60°C as a function of temperature at 1 Hz. show a single relaxation associated with the Kraton glass transition.
Figure 2. Shear storage ($G'$), shear loss ($G''$) moduli, and tan delta of X-0287 aged 3 years at 60°C as a function of temperature at 1 Hz. show two \textit{cor} relaxations: a glass transition from Kraton at -45°C and the melting transition of the R2-170 wax additive.
Figure 3. An Arrhenius relationship was found between the random scission rate constant for degradation of oil-extended Kraton binder (open circles) and accelerated aging temperature. The wax additive (squares) reduced Kraton degradation for isothermal conditions below the wax melting point.