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THE DETERMINATION OF BINDER DEGRADATION IN PLASTIC-BONDED EXPLOSIVES

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ABSTRACT

In this paper we describe how molecular-size-distribution measurements made by gel-permeation chromatography can be used to detect degradation in the binder systems of plastic-bonded explosives. The procedures for sample preparation and chromatographic analysis are outlined. Several examples are given to illustrate the usefulness of this method for studying the stabilities of a variety of explosives systems.

1. INTRODUCTION

The binder systems in many plastic-bonded explosives (PBX's) are plasticized with highly mobile, low-molecular-weight compounds of limited stabilities, and frequently the polymers in these systems contain bonds that are readily susceptible to attack. Consequently, there is considerable uncertainty about how well the binder components of PBX's can withstand long exposures to elevated temperatures. Main-charge explosives like HMX or RDX, on the other hand, are thought to be sufficiently stable to meet current requirements.

In the past, we have utilized many methods to detect degradation or changes in PBX systems. These techniques, including evolved-gas analyses, weight and density measurements, DTA, DSC, TGA and vacuum-stability tests, measure properties or behavior of the system as a whole; they do not directly examine the area that we now feel is the main source of trouble, structural degradation in the binder. Only recently have we directed much attention to methods for detecting and analyzing binder degradation.

We have been able to demonstrate that binder degradation can be characterized by measuring the changes that occur in the molecular sizes of the binder components with gel-permeation chromatography (GPC). With this method, we can detect changes in binder structure as distinct from those in the explosive or other components. In the following sections of this paper, we describe the analytical details of this method and offer a few examples to illustrate its utility.

2. EXPERIMENTAL PROCEDURES

The binders were separated from the explosives systems by solvent extraction. (The preferred solvent for this work is 1,2-dichloroethane because of the low solubility of HMX.) A 0.5-g sample of crushed PBX, 5 ml of solvent and four 4 mm glass beads were placed in a 10-ml volumetric

flask. The flask was shaken for a 24-hr period to ensure dissolution of the binder components, then the liquid phase was separated from the residual solid materials by centrifugation. The extract was diluted to 40 vol% with tetrahydrofuran (THF). A 1-ml aliquot of this solution was subjected to GPC analysis.

GPC analyses were done with a Waters Model 200 gel-permeation chromatograph. The chromatograph was equipped with two column sets that could be used alternately. For high-molecular-weight materials, we used the large-pore column set, consisting of five 1.2 m polystyrene columns connected in series and having porosities of 10^6, 10^5, 3×10^4, 10^4 and 900 Å. Low-molecular-weight compounds were analyzed with a similar arrangement of columns; however, column porosities were 3×10^3, 500, 250, 250 and 60 Å. THF, flowing at 1 ml/min, was used as the chromatographic solvent. Sample injection times varied between 10 and 90 s, depending on the sensitivity of the detector for the materials being analyzed. Results were recorded as the change in refractive index as the chromatographed sample passed through the detector. The relative concentration in any given elution volume is directly proportional to the change in refractive index.

3. RESULTS AND DISCUSSION

An excellent example of the usefulness of GPC for detecting binder degradation was provided by a recent study of the long-term stability of PBX X-0242.* A series of X-0242 samples had been stored in sealed glass ampoules in Ar at 75°C for various periods of time. After 64 weeks of storage, a total of only 0.6 cm^3 of gas had evolved per g of sample. There were no appreciable weight losses or density changes in any of the samples. Gas chromatography revealed that a small loss of nitroplasticizer had occurred during storage, but an infrared spectrum of the polyurethane failed to detect any substantial structural changes. However, we found that the compressive strengths of these samples had progressively decreased as a function of storage time. After 64 weeks, the X-0242 test samples retained only about one-third of their original strengths. The reason for this degradation was provided by GPC analyses of the molecular-size distributions of the binders in the surveillance samples.

In Figure 1, we have reproduced the GPC curves for the binder systems of several X-0242 samples. The continuous curve was obtained from a reference sample composed of equal amounts of Estane and nitroplasticizer. Estane, which has a peak molecular weight of about 50,000, is seen to have a broad molecular-size distribution. The nitroplasticizer peak, on the left side of the GPC curve, is clearly separated from the Estane region. The GPC curves for the 32- and 64-week samples show beyond a doubt that severe Estane degradation has occurred as a result of the storage conditions. The average molecular weight of the Estane in the 64-week sample is down to approximately 2,000. This degradation in the polymeric binder component is the cause for the loss of sample compressive strength. Interestingly, as Fig 1 also illustrates, the Estane in a newly prepared sample (X-0242 control) was found to be partially degraded. This shows

*PBX X-0242 is composed of 95 wt% HMX, 2.5 wt% polyurethane (Estane) and 2.5 wt% nitroplasticizer [a 50/50 mixture of bis(2,2-dinitropropyl)formal and bis(2,2-dinitropropyl)acetal].

that the first bond cleavages in the polymer take place during the preparation or fabrication of the explosives system.

The results obtained for the X-0242 system amply illustrate the pitfalls of attempting to evaluate PBX stabilities or compatibilities without sufficient information about what is happening to the individual components. Without recourse to the molecular-size analyses, grossly erroneous conclusions about the stability of the PBX could have been made.

Another explosives system of interest to many is PBX 9404.* A GPC curve of the binder from a reference sample of this PBX is given in Fig 2. The nitrocellulose peak appears on the right side of the trace, and the CEF is seen as a shoulder on the lower-molecular-weight side of the larger HMX peak. HMX appears in this GPC curve because ethyl acetate, rather than dichloroethane, was used in the initial extraction.

GPC was used to examine binder samples from both the center and the surface of a block of PBX 9404. This material had been stored in a sealed container with several other plastic and metal components for approximately 1.5 years at 49°C. Although a relatively large amount of plasticizer appeared to be present, we found the binder from the center of the surveillance sample to be in good condition, as shown by the GPC trace in Fig 3. However, the nitrocellulose is seen to be absent altogether from the GPC curve of the binder removed from the surface (Fig 4). These observations indicate that the nitrocellulose was depleted at the surface either by migration or reaction during storage; however, it is possible that it crosslinked and was no longer soluble in the extraction solvent.

A final example of the use of GPC for analyzing binder degradation in explosives system is provided by our experience with a surveillance sample of PBX X-0234.** A GPC curve of a X-0234 reference sample is shown as the continuous trace in Fig 5. The acrylate polymer in this explosive has been poorly polymerized, shown by the low-molecular-weight tail extending all the way to the CEF peak. The dashed curve was obtained from the binder in an X-0234 sample that had been stored for just 4 weeks at 75°C. Here, as in the 9404 case just discussed, the polymeric component was found to be largely absent from the GPC curve; however, prior experience with another explosive similar to X-0234 suggests that the acrylate polymer in the surveillance sample was crosslinked during storage, rendering it insoluble.[1]

The foregoing examples have demonstrated that binder degradation in a variety of explosives systems can be detected by measuring changes in the molecular-size distributions of the binder components with gel-permeation chromatography.

4. REFERENCES

(1) Private Communication with D. Seaton, LLL.

*The composition of PBX 9404 is: 94 wt% HMX, 2.9 wt% nitrocellulose, 2.9 wt% tris(chloroethyl)phosphate (CEF) and 0.2 wt% diphenylamine.

**PBX X-0234 is composed of 94 wt% HMX, 3.6 wt% dinitropropyl acrylate polymer and 2.4 wt% CEF.

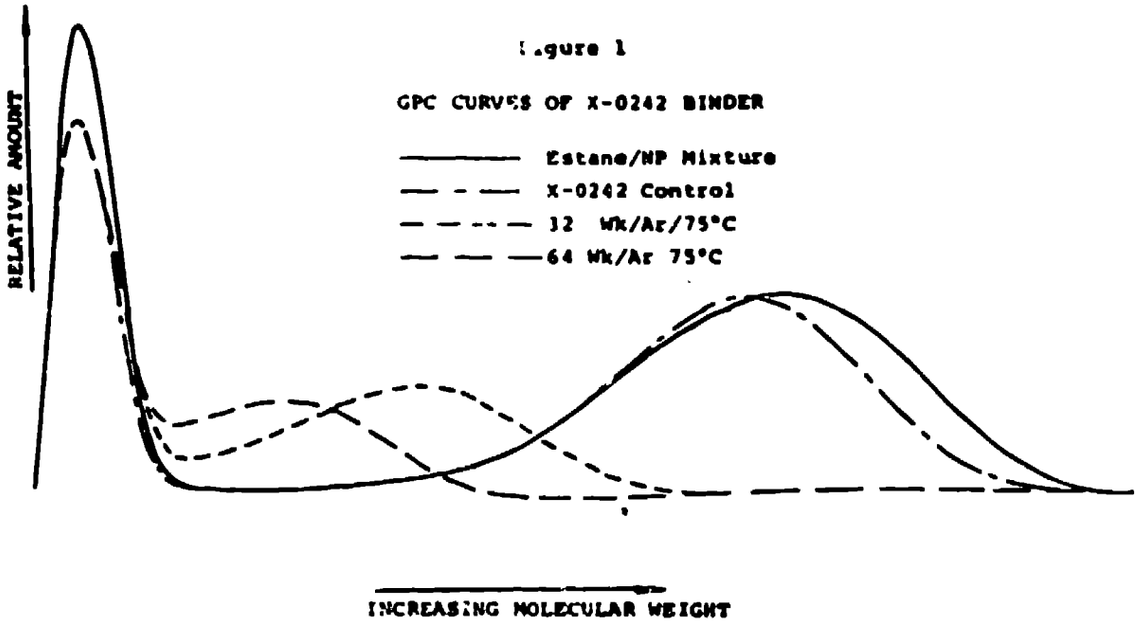


Figure 1

GPC CURVES OF X-0242 BINDER

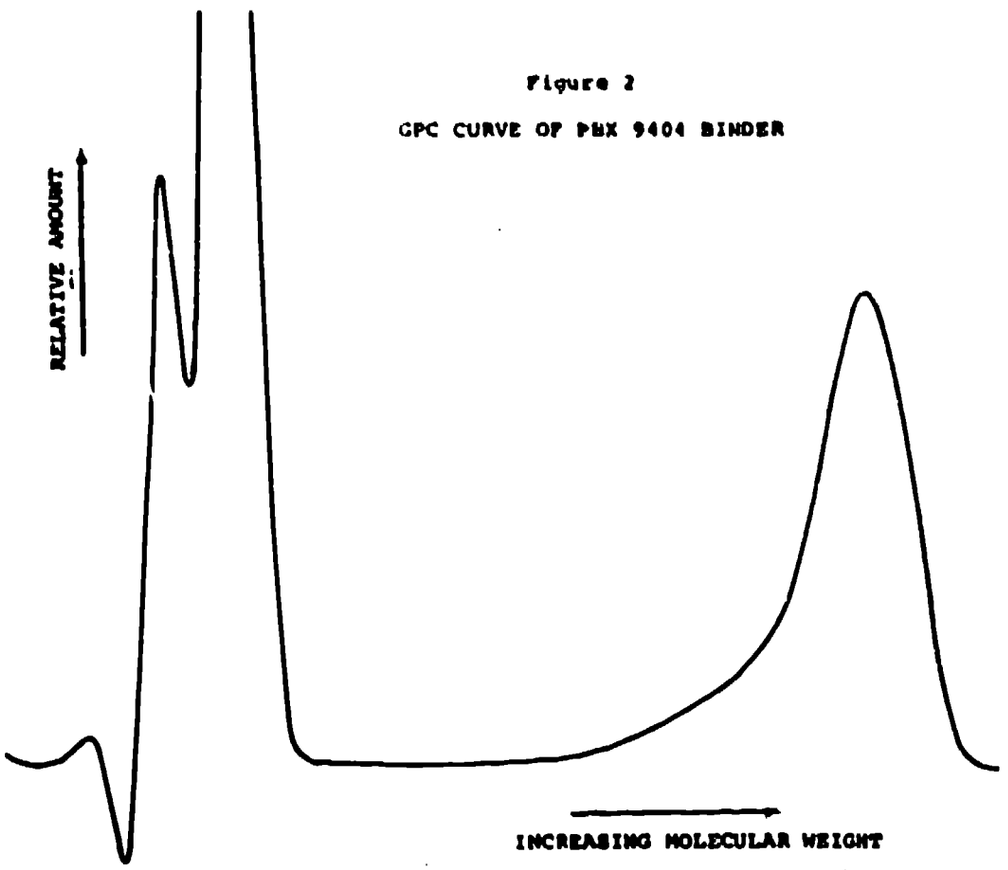


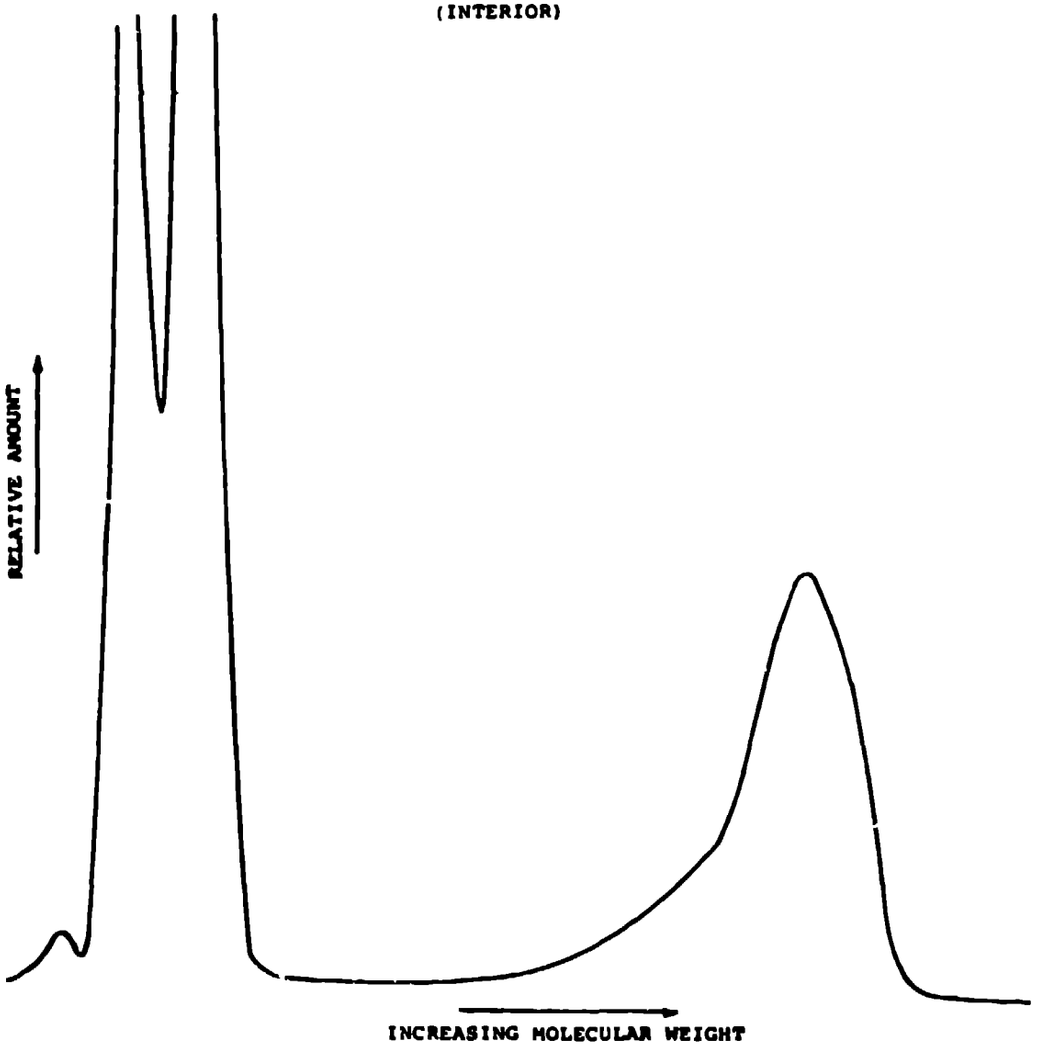
Figure 2

GPC CURVE OF PBX 9404 BINDER

Figure 3

PBX 9404 SURVEILLANCE SAMPLE

(INTERIOR)



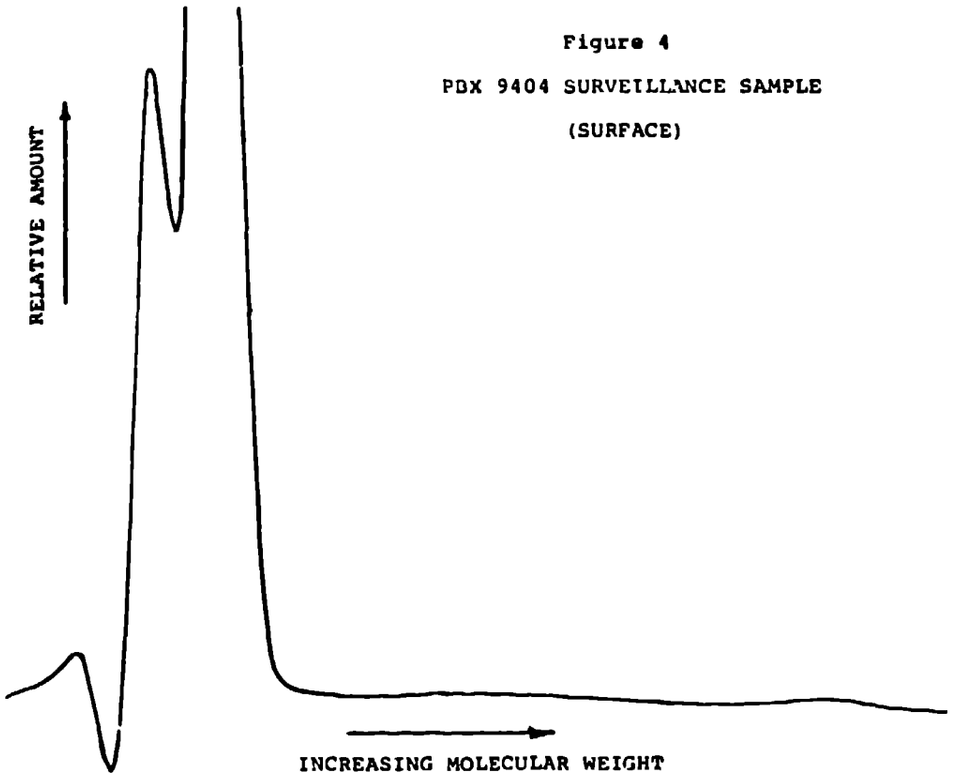


Figure 4

PBX 9404 SURVEILLANCE SAMPLE

(SURFACE)

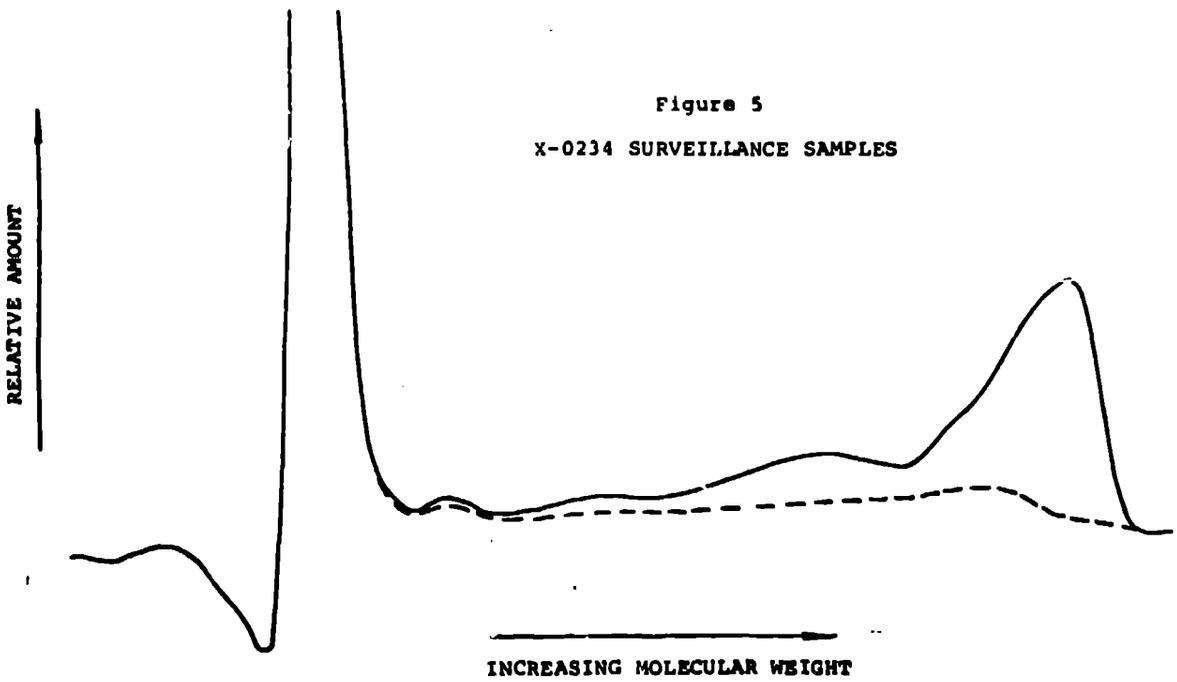


Figure 5

X-0234 SURVEILLANCE SAMPLES