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DETERMINATION OF TRACE AMOUNTS OF EASTMAN 910 ADHESIVE
IN CERTAIN PLASTIC-BONDED EXPLOSIVES

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SUMMARY

A pyrolytic gas chromatographic method for determining small amounts of Eastman 910 polymer in certain plastic-bonded explosives is described. The Eastman 910 polymer is separated from the plastic-bonded explosives by solution in nitromethane-chloroform, and an aliquot of the solution is converted to the monomer, methyl 2-cyanoacrylate, by controlled pyrolysis for gas chromatographic analysis. The peak area of the monomer is related to polymer concentration by means of a calibration curve. It is shown how the method may be used to study the penetration of the adhesive into glued pellets of the explosive.

INTRODUCTION

When adhesives are used with porous substrates, questions frequently arise concerning the extent to which the adhesive penetrates the substrate. Such penetration may affect the strength of the bond and may alter the properties of the substrate in the region adjacent to the bond. In this paper we describe an application of pyrolytic gas chromatography to a particular problem of this type, namely, the determination of small amounts of Eastman 910 adhesive (methyl 2-cyanoacrylate polymer) in certain plastic-bonded explosives (PBX). Eastman 910 is frequently the adhesive of choice for use with explosives, as, for example, when it is desired to glue a pressed PBX charge to a metal plate to obtain intimate contact at the interface.

A recent publication by the author¹ showed that cured Eastman 910 pyrolyzes to methyl 2-cyanoacrylate monomer as its characteristic product. Under controlled pyrolysis, it was found that the monomer yield was proportional to the polymer concentration. However, when PBX is present, the explosive component interferes. Interference is minimized by preferentially dissolving the Eastman 910 in a nitromethane-chloroform mixture and taking an aliquot of the solution for analysis. Good results were obtained with synthetic samples and with PBX 9010 and PBX 9407 samples contaminated with the adhesive.

MATERIALS AND METHODS

Materials, equipment and reagents

PBX 9010 is 90/10 RDX (hexahydro-1,3,5-trinitro-s-triazine)/Kel-F 3700 elastomer (3 M Co.). PBX 9407 is 94/6 RDX/Exon 461 (Firestone Plastics Co.). Composition B-3 is 60/40 RDX/TNT (trinitrotoluene).

A Perkin-Elmer pyrolysis unit, an Aerograph hi-fi Model 600-D gas chromatograph, and a Varian Model G-14 recorder were used.

A 1-ft.-long by 1/8-in.-O.D. (0.094-in.-I.D.) stainless-steel tube was packed with 25% (by weight) of diisodecyl phthalate on 60-80 mesh, acid-washed Chromosorb W, using a Matronic XL-300 column packer. The packed column was preconditioned with helium carrier gas at 125° for 24 h before use.

Liquid Eastman 910 adhesive, purchased from Eastman Chemical Products, Inc., was distilled twice under vacuum and the distillate was polymerized in water. The dried polymer had an indicated purity of 99.2% from C, H, and N analyses.

Six 1-ml and 10-ml volumetric flasks, two Hamilton microsyringes (10 μ l capacity), and twelve micro porcelain combustion boats (No. 00000) were required. An ultrasonic shaker and a centrifuge were used for sample preparation.

Experimental

Several partitioning columns were prepared and tested for their ability to separate methyl 2-cyanoacrylate monomer from other pyrolysis products. The 1-ft. 25% diisodecyl phthalate column was found to work satisfactorily. At a column temperature of 80° and a flow rate of 32-33 cm³/min of hydrogen carrier gas, methyl 2-cyanoacrylate elutes completely from the column in about 11 min as a reasonably symmetrical peak acceptable for area measurement. The conditions necessary to optimize the yield of the monomer with this column were investigated.

Fig. 1 shows the dependence of the monomer yield on the pyrolysis temperature. The maximum occurs between 250 and 270°, which is much lower than the optimum ranges for polystyrene (500 to 525°) and Estane 5740 X2 (600°), which we have studied previously^{2,3}.

The influence of the hydrogen flow rate on the monomer yield is shown in Fig. 2 for two different pyrolysis temperatures. At flow rates of 25-35 cm³/min, a broad maximum is observed; however, at about 25 cm³/min peak broadening occurs. Therefore, a flow rate of 32-33 cm³/min was chosen for our work.

Three explosives (PBX 9010, PBX 9407, and Composition B-3) were studied in mixtures with Eastman 910. At a pyrolysis temperature of 260° and with the gas chromatographic conditions given in Fig. 1, mixed samples were pyrolyzed to study monomer recovery. With increasing amounts of explosive, the recovery of the monomer decreased markedly. Consequently, a solvent was sought to dissolve the polymer preferentially so that the explosive would not interfere with the analysis. As a further precaution, the pyrolysis temperature was lowered. Treatment of the mixed sample with nitromethane and chloroform and the lowering of the pyrolysis temperature to 200° worked with PBX 9010 and PBX 9407 containing trace amounts of Eastman 910. Mixtures of Composition B-3 and Eastman 910, however, could not be analyzed by this method, because TNT dissolves readily in the solvent and interferes with the analysis.

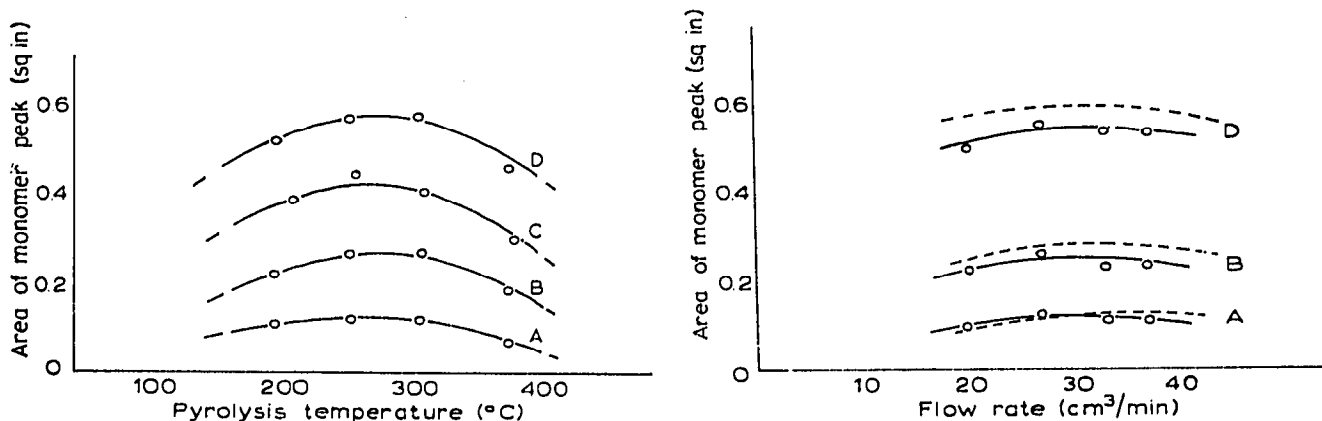


Fig. 1. Effect of pyrolysis temperature on the yield of Eastman 910 monomer. Chromatographic conditions: Column, 1 ft. long by 1/8 in. O.D. (0.094 in. I.D.); 25% diisodecyl phthalate on 60-80 mesh, acid-washed Chromosorb W. Column temp., 80°; inlet temp., 100°; hydrogen carrier gas, flow rate 32-33 cm³/min; recorder speed, 16 in./h; electrometer range 0.1; attenuation $\times 16$. Sample size: curve A = 0.5 μ g Eastman 910 polymer; curve B = 1.0 μ g Eastman 910 polymer; curve C = 1.5 μ g Eastman 910 polymer; curve D = 2.0 μ g Eastman 910 polymer. Each point represents an average of three runs.

Fig. 2. Effect of hydrogen flow rate on yield of Eastman 910 monomer. Chromatographic and pyrolysis conditions: chromatographic conditions same as in Fig. 1, except variable flow rates. Pyrolysis temp., - - - - = 260°; ——— = 200°. Sample size: curve A = 0.5 μ g Eastman 910 polymer; curve B = 1.0 μ g Eastman 910 polymer; curve D = 2.0 μ g Eastman 910 polymer. Each point represents an average of three runs.

Procedure

A 0.05-0.1 g sample of explosive contaminated with Eastman 910 is dispersed in 0.25 ml of nitromethane with an ultrasonic shaker for 10-15 min. The solution is diluted to 1 ml with chloroform and then centrifuged to separate the undissolved explosive. With the Hamilton microsyringe, 2-5 μ l of the solution is transferred into a micro porcelain combustion boat and the sample is evaporated to dryness at room temperature. Up to six boats with samples are loaded into the pyrolysis unit, and the flow rate of the hydrogen carrier gas is adjusted to 32-33 cm³/min at a column temperature of 80°. After the recorder is turned on and the electrometer is balanced, the flame detector is ignited. The sample is moved into the pyrolysis chamber, maintained at 200°, with a magnet and boat-pusher. The pyrolysis products are separated on a 1-ft. diisodecyl phthalate column. The area of the methyl 2-cyanoacrylate peak is measured by the (peak height) \times (peak width at half-height) method and related to polymer concentration by means of a calibration curve.

RESULTS AND DISCUSSION

Typical pyrograms of synthetic PBX samples are shown in Figs. 3A and B. With mixed-sample pyrolysis, the methyl 2-cyanoacrylate peak appears on the trailing edge of the PBX pyrolysis products; however, area measurements by planimeter and by the (peak height) \times (peak width at half-height) method gave identical results.

The results obtained with synthetic samples and authentic glued samples of PBX 9010 and PBX 9407 are summarized in Table I. The standard deviations are

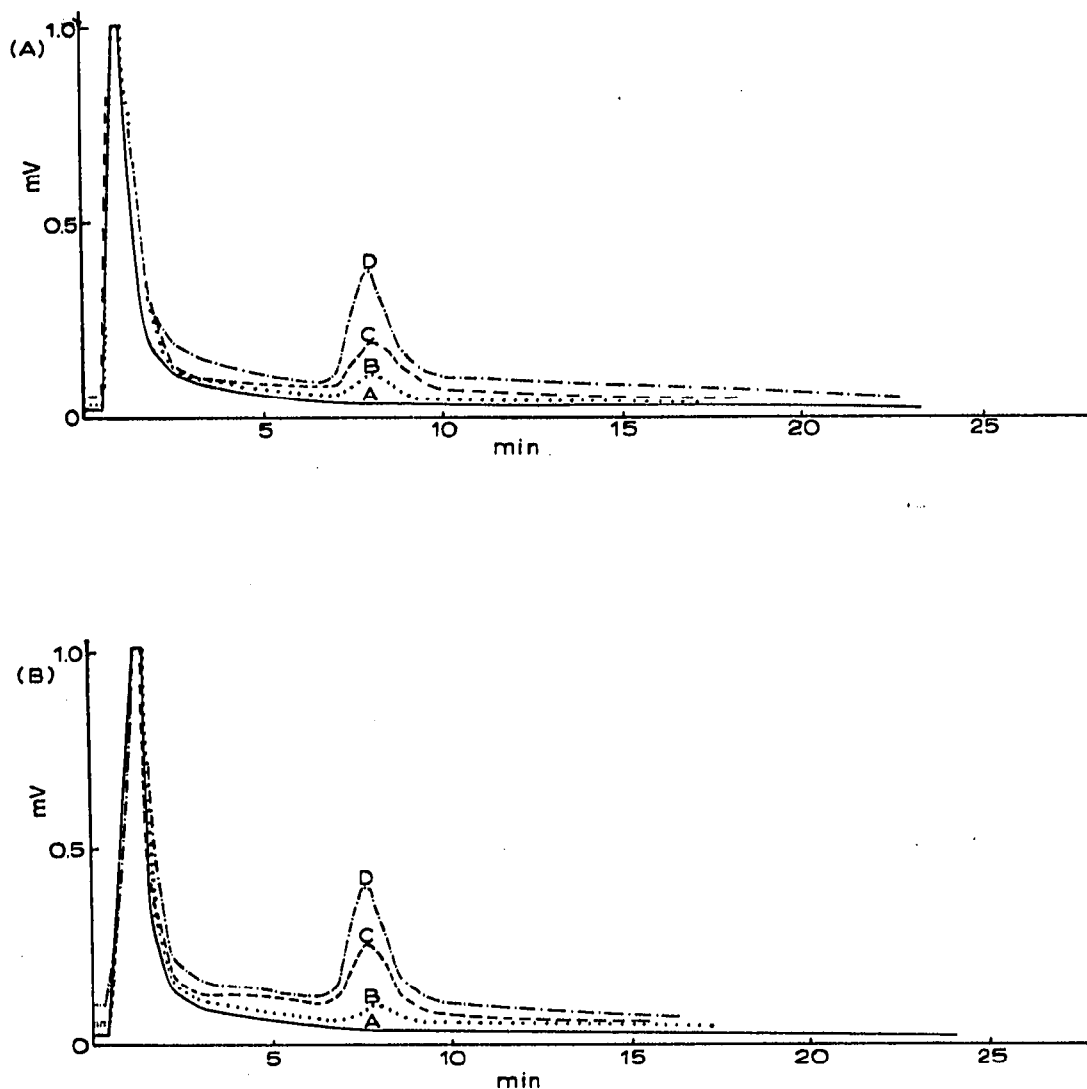


Fig. 3. (A) Pyrograms of synthetic samples of Eastman 910-PBX 9010. Chromatographic and pyrolysis conditions: Column, 1 ft. long by 1/8 in. O.D. (0.094 in. I.D.); 25% diisodecyl phthalate on 60-80 mesh acid-washed Chromosorb W. Column temp., 80°; inlet temp., 100°; hydrogen carrier gas, flow rate 32-33 cm³/min; recorder speed, 16 in./h; electrometer range 0.1; attenuation $\times 8$; pyrolysis temp., 200°. Sample size: curve A = 5 μ l CH₃NO₂-CHCl₃ solution saturated with PBX 9010; curve B = 5 μ l 0.026% synthetic sample = 0.13 μ g 910 polymer; curve C = 5 μ l 0.052% synthetic sample = 0.26 μ g 910 polymer; curve D = 5 μ l 0.090% synthetic sample = 0.45 μ g 910 polymer. Peaks B, C, and D are methyl 2-cyanoacrylate monomer.

(B) Pyrograms of synthetic samples of Eastman 910-PBX 9407. Chromatographic and pyrolysis conditions same as for (A). Sample size: curve A = 5 μ l CH₃NO₂-CHCl₃ solution saturated with PBX 9407; curve B = 5 μ l 0.022% synthetic sample = 0.11 μ g 910 polymer; curve C = 5 μ l 0.053% synthetic sample = 0.27 μ g 910 polymer; curve D = 5 μ l 0.100% synthetic sample = 0.50 μ g 910 polymer.

excellent, though the average values appear to be systematically low by a small amount for the synthetic samples. The glued PBX 9407 pellets (1/16-in. thick by 1/4-in. diam.), which were simply pried off the surface to which they were glued, contain 0.47 to 0.78% Eastman 910. The variation in the polymer content is due to the varying amounts of adhesive originally applied at the glue-bond surface. PBX 9010

TABLE I

ANALYSIS OF EASTMAN 910 POLYMER IN PBX MIXTURES

<i>Sample</i>	<i>Ratio of composition</i>	<i>No. of det'ns</i>	<i>910 polymer found (%)</i>	<i>Std. dev.</i>
Synthetic mix	0.40/100-910 polymer/PBX 9010	5	0.37	0.02
Synthetic mix	0.09/100-910 polymer/PBX 9010	5	0.08	0.01
Synthetic mix	0.05/100-910 polymer/PBX 9010	5	0.05	0.00
Synthetic mix	0.03/100-910 polymer/PBX 9010	5	0.02	0.00
Synthetic mix	0.50/100-910 polymer/PBX 9407	5	0.50	0.03
Synthetic mix	0.10/100-910 polymer/PBX 9407	5	0.10	0.01
Synthetic mix	0.05/100-910 polymer/PBX 9407	5	0.05	0.01
Synthetic mix	0.02/100-910 polymer/PBX 9407	5	0.02	0.01
PBX 9407, glued pellet	—	5	0.47	0.04
PBX 9407, glued pellet	—	7	0.78	0.04
PBX 9407, glued pellet	—	5	0.58	0.02
PBX 9407, glued pellet (top half away from glue bond)	—	6	0.15	0.02
PBX 9407, glued pellet (top half away from glue bond)	—	5	0.06	0.00
PBX 9407, glued pellet (top half away from glue bond)	—	5	0.09	0.01
PBX 9010, glued slab	—	5	0.07	0.01
PBX 9010-Sample A (first 1/16 in.)	—	6	0.43	0.04
PBX 9010-Sample B (next 1/8 in.)	—	5	0.00	0.00
PBX 9010-Sample C (remainder of pellet)	—	5	0.00	0.00

(about 3/8-in. thick) glued to an aluminum shell shows 0.07% of the Eastman 910 polymer.

To study the penetration of Eastman 910 into the PBX, glued samples were sectioned for analysis. With PBX 9010, sample A consisted of a 1/16-in.-thick layer adjacent to the glue-bond surface, sample B the next 1/8-in. layer, and sample C the remaining portion of the PBX 9010. With PBX 9407, three pellets were sectioned, and the top half of the pellet, furthest from the glue bond, was analyzed. The results are shown in Table I.

It can be seen that, with PBX 9010, the Eastman 910 penetrated no more than 1/16 in. into the sample. With PBX 9407, the amount of Eastman 910 found in the top half of the pellets varied from 0.06 to 0.15%, so that the glue penetrated at least 1/32 in. into the pellets.

ACKNOWLEDGEMENT

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