

EXPLOSIVE COMPATIBLE POLYMERS FOR DEFENSE APPLICATION

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ABSTRACT

A paper study was conducted to determine the probable compatibility of several classes of thermosetting polymer systems with explosives. The chemical reactivity of explosive materials with the more common thermosetting resins is discussed. The most common test procedures to detect chemical instability of explosives with other materials are reviewed.

1. INTRODUCTION

In many defense-oriented applications, the use of thermosetting polymer systems involves contact between polymers and explosives. A paper study was conducted examining the compatibility of a variety of polymers with explosives. Critical parameters when considering the use of thermosetting polymers are their set time, strength, modulus, adhesion, and ease of use. An optimum material should normally be easy to deploy, should rapidly reach a rigid state, have high strength without being brittle, and should adhere well to a variety of metallic and nonmetallic materials.

The requirement for compatibility of the polymeric system is probably the most restrictive when the variety of energetic materials are considered. A majority of the materials in the explosive train are encased for ease of handling and protection from the elements. However, in accidents explosive devices may sustain damage, exposing the energetic components to environments other than those encountered during normal storage, and to materials not normally contacted.

A defense mission requires a stringent definition of the term "incompatible". The definition follows: (1)

- (1) A chemical reaction between the additive and the components of the explosive which gives rise

to a significant increase in sensitivity, decrease in thermal stability, or the chemical destruction of one or more components of the explosive.

- (2) Migration of an explosive component into an adjoining substrate, leading to changes in mechanical, physical or explosive properties in either the explosive or substrate.
- (3) The formation of a low-melting eutectic which may exude during high-temperature storage.

2. DISCUSSION

2.1 CHEMICAL REACTIVITY OF FUZE TRAIN EXPLOSIVES

The reactivity of explosives with other chemicals or materials encountered is of concern because of the possible destructive effects of an autocatalytic reaction.

2.1.1 Aromatic C-Nitro Compounds

TNT: 2,4,6-Trinitrotoluene. TNT is relatively nonreactive, but it can form compounds by either association or reaction. With basic compounds such as aniline, pyridine, diphenylamine, the naphylamines, the toluidines and carbazole, it forms molecular compounds having characteristic colors and melting

points. Alkalis, alkoxides and ammonia react with TNT to form dangerously sensitive compounds.

TNT, like other highly nitrated aromatic hydrocarbons, easily forms addition products with polycyclic hydrocarbons and amines. Aromatic nitro compounds react with free radicals, thus explaining the inhibiting effect on addition polymerization of vinyl compounds.

DIPAM: 3,3'-Diamino-2,2',4,4',6,6'-Hexanitrobiphenyl, and HNS: 2,2',4,4',6,6'-Hexanitrostilbene. The reactivity of both DIPAM and HNS with alkalis and bases should be about the same as TNT although neither explosive contains an activated methyl group as in TNT. Although DIPAM contains two amino groups, the electron withdrawing effect of the nitro groups causes the compound to be somewhat acidic.

2.1.2 Aminoguanidine Derivatives

Tetracene: 4-Guanyl-1-(nitrosoaminoguanyl)-1-tetrazene. Boiling water decomposes tetracene, liberating nitrogen. It is hydrolyzed by sodium hydroxide, yielding ammonia and cyanamide among the products. Tetracene reacts with an excess of silver nitrate to form a double salt, and forms explosive salts such as perchlorate.

2.1.3 Chlorates

Potassium Chlorate: $KClO_3$. Pure $KClO_3$ has no explosive properties, but when used in a mixture with fuels such as sugar, starch, or aluminum powder it forms an explosive highly sensitive to mechanical action, especially friction. It is known that ammonium salts (e.g. ammonium nitrate) must not be added to chlorate compositions since a double exchange reaction may occur, resulting in the formation of ammonium chlorate, an unstable compound which decomposes spontaneously.

2.1.4 Diazo Compounds

DDNP; Diazodinitrophenol: 4,5-Dinitrobenzene-2-diazo-1-oxide. A diluted solution of sodium hydroxide decomposes DDNP, liberating nitrogen. DDNP is not decomposed by concentrated acids at room temperature.

Lead Azide: $Pb(N_3)_2$. Lead azide, like hydrazonic acid, can undergo oxidation and reduction reactions. Lead azide is decomposed by a 10 percent solution of sodium hydroxide, forming lead hydroxide and sodium azide. When dissolved in aqueous ammonium acetate, lead azide reacts with potassium dichromate to form

potassium azide and lead chromate.

2.1.5 Nitramines

RDX; Cyclotrimethylenetrinitramine: Hexahydro-1,3,5-trinitro-S-triazine. RDX is hydrolyzed slowly when treated with boiling, dilute sulfuric acid or sodium hydroxide, yielding ammonia, formaldehyde and nitric acid. It is reduced when dissolved in hot phenol, yielding methylamine, nitrous acid and hydrocyanic acid.

HMX; Cyclotetramethylenetetranitramine 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane. The chemical reactivity of HMX is similar to that of RDX. HMX is more resistant to decomposition by sodium hydroxide than RDX.

Tetryl: 2,4,6-Trinitrophenylmethylnitramin. Tetryl reacts with aqueous alkali to yield metallic picrates, nitrites and methylamine. When tetryl is boiled in a solution of sodium carbonate, or potassium, or sodium hydroxide, the nitramino group is hydrolyzed. The products are picric acid, methylamine and nitrous acid. When heated with alcoholic ammonia, a picramide is formed. Tetryl reacts with aniline in benzene solution even at room temperature to form 2,4,6-trinitrodiphenylamine and methylnitramine.

2.1.6 Nitrate Esters

PETN: Pentaerythritol Tetranitrate. Due to its symmetrical structure, PETN is highly resistant to many reagents. Thus PETN, differing from most nitric esters, is not readily decomposed by sodium sulfide at $50^\circ C$. But it is decomposed rapidly by boiling in a ferrous chloride solution.

2.1.7 Nitrophenol Salts

Lead Styphnate, Lead 2,4,6-trinitroresorcinate. Lead styphnate is decomposed by concentrated nitric or sulfuric acid. When dissolved in ammonium acetate solution, it reacts with potassium dichromate to form potassium styphnate and lead chromate. Neutral lead styphnate reacts at $50^\circ C$ with pyridine to form an addition product.

2.2 THERMOSETTING POLYMERS

The term "polymer" refers to a large molecule made of many simple repeating units. Network or crosslinked polymers arise when polymer chains are chemically linked. Because of crosslinking, the polymer chains lose their mobility and the material has dimensional stability and can be considered one giant molecule.

A thermoset polymer will not melt or flow, and cannot be molded. When using thermosetting resins, one must accomplish the crosslinking reaction in place.

2.2.1 Epoxy Resins

The term "epoxy" refers to a chemical group consisting of an oxygen atom bonded to two carbon atoms already united in some other way.

For the purposes of this paper, an epoxy resin is defined as any molecule containing more than one α -epoxy group capable of being converted into thermoset form. The term is also used to indicate the resins in both the thermoplastic (uncured) and thermoset (cured) states.

The first commercial epoxy resins were the reaction products of epichlorohydrin and bisphenol A to give the diglycidyl ether of bisphenol A (DGEBA). Via the epichlorohydrin route a large number of other epoxy resins are made by reaction with other compounds containing active hydrogens. These may include organic and inorganic acids, nitrogen-containing compounds, and silicones. Monoepoxides other than epichlorohydrin can also be used to synthesize these resins. Another major class of epoxy resins is made by the epoxidation of olefins, and from acetyl compounds. (2)

The popularity of epoxy resins is due to a unique combination of desirable properties. These include low viscosity, good cure properties, relatively low shrinkage, excellent adhesive properties, high mechanical strength, and a high degree of versatility and chemical resistance. The conversion of a liquid epoxy resin to a hard, thermoset solid is accomplished by the addition of a chemically active curing agent. The conversion from liquid to solid usually does not generate any by-products.

There are mainly two general classes of curing agents--acids and bases. The basic curing agents are usually amines, amides, Lewis bases and inorganic bases. Acid curing agents usually employed are Lewis acids, carboxylic acid anhydrides, organic acids, and phenols. It has been shown previously that bases are incompatible with most explosives. It has been amply demonstrated experimentally that amine curing agents are not compatible with most explosives. Amine-cured epoxy resins may or may not be compatible with explosives even after cure is assumed complete. (3,4,5) Some of the contributing factors are type and basicity of amine, mechanism of cure, and structure of the cured resin. Therefore, if epoxy

resins are to be used in contact with explosives, acidic curing agents should be used.

2.2.2 Polyurethanes.

The basic chemistry of the polyurethanes is that one mole of a diisocyanate reacted with one mole of a difunctional hydrogen donor will polymerize into a solid mass. No by-products are evolved unless water or a carboxyl group is present, in which case carbon dioxide gas is given off.

2.2.3 Vinyl Polymers and Unsaturated Polyesters

These polymers are usually crosslinked via a free-radical reaction with organic peroxides, the usual source of radicals. Since nitrocompounds react with free radicals, and TNT is incompatible with peroxides, this type of polymer does not seem useful.

2.2.4 Polysiloxanes (Silicones)

This group of commercially useful polymers has been used to a limited extent in warheads. Silicone resins usually have low reactivity and must be cured at elevated temperatures. Silicone rubbers (RTV) will cure at room temperature, but long gel times at low temperatures can be expected. Other problems likely to be encountered are very high viscosities at low temperatures and short shelf-life at moderate temperatures. However, silicone systems can be devised which should be compatible with most explosives. Silicone diluents are available which will lower the viscosity of silicone polymers at low temperatures, and more reactive curing agents may lower the gel time to acceptable levels.

2.3 TEST METHODS FOR EVALUATING COMPATIBILITY OF MATERIALS WITH EXPLOSIVES

Thermal and chemical decomposition kinetics of most explosives are extremely complex and their reaction mechanisms are not clearly understood. Therefore, the most common analytical techniques for determining chemical and thermal explosive compatibilities are largely based on empirical methods. A major weakness of these tests is that they provide no indication of the type of reaction occurring, or of the reaction products formed. It is often difficult to predict the relative compatibility of explosive mixtures over long periods at lower temperatures based on the data obtained from accelerated tests at higher temperatures. Scaling effects are important but are difficult to predict from small-scale tests.

A large number of techniques and test procedures have been used to detect instability of explosives in contact with other materials. Some of the more common ones are given below.

2.3.1 Differential Thermal Analysis (DTA)

DTA is one of the more commonly used techniques in stability testing. The temperature of the explosive sample is measured and compared to a thermally inert reference material heated and cooled under the same conditions. The DTA method is used to detect thermal changes or transitions. The usual changes observed are chemical reactions and phase transitions such as vaporization, fusion, and glass transitions in polymers. (6,7)

2.3.2 Differential Scanning Calorimetry (DSC)

DSC overcomes the disadvantages of conventional DTA equipment. Although sample and reference material are subjected to increasing or decreasing temperatures as in DTA, an additional control system detects any difference between sample and reference temperature, and changes heat applied to maintain both at the same temperature. DSC measures the difference in electrical power required to maintain sample and reference material at the desired temperature, and provides information on changes in chemical state and exothermic or endothermic chemical changes. (8)

2.3.4 Thermal Gravimetric Analysis (TGA)

TGA measures the weight loss as a sample is heated.

2.3.5 Mass Spectrometry

Mass spectrometry is a means of separating and determining the relative abundance of ions of different mass-to-charge ratio produced by bombarding the sample with electrons. It has the distinct advantage of identifying reaction products and characterizing starting materials, and thus provides more useful information than more empirical methods of incompatibility testing. (8)

2.3.6 Gas Chromatography

Gas Chromatography is a means of analyzing gases evolved after accelerated thermal aging of an explosive sample. (8,10-14) Should volatile decomposition products be formed, they can be separated, identified, and measured with the gas chromatograph. The

use of a mass spectrometer in conjunction with the gas chromatograph is highly recommended for compatibility testing.

2.3.7 Thin Layer Chromatography (TLC)

This is a micro type of chromatography in which a thin layer, usually silica gel spread on glass plates or plastic film, is the absorbent. Drops of test solutions are placed along one edge of a coated plate, and this edge then dipped into a solvent. The solvent carries the constituent of the test solution up the thin layer in a selective separation, so that various identifying tests can be carried out. Both qualitative and quantitative analyses of explosives can be carried out by TLC. Purity and amount of thermal degradation of explosives have been assessed by this method. The compatibility of explosive mixtures, after some accelerated heating cycle, can also be determined. This method is especially useful if solid decomposition products are formed. (15-24)

2.3.8 The Vacuum Stability/Compatibility Test

The test sample is heated in an evacuated system and the volume of evolved gases is measured over a standard time period and temperature. To determine compatibility of an explosive with an additive, separate runs are made with the additive, the explosive and the mixture. A chemical reaction is indicated if the gas volume of the mixture is greater than the sum of the gas volumes of the inert and explosive samples.

The vacuum stability/compatibility test has not been standardized. Temperatures of 90°, 100° and 120°C, time periods of 40 and 48 hours, and different sample weights are used by different laboratories. The Navy standardized both the vacuum stability and explosive compatibility tests. The standard tests will appear in the revision of Reference 14. A complete description of the vacuum stability apparatus and the procedure used by the Naval Surface Weapons Center is given in Reference 25. Similar tests for stability and compatibility are given in References 26 and 27.

The vacuum stability/compatibility test has a number of shortcomings. The method is empirical and based on unvalidated assumptions that incompatibility will result in the formation of noncondensable gases. For a given system this may or may not be true. The test provides only fair reproducibility, especially from laboratory to laboratory. It is slow (48 hours) and the equipment is cumbersome.

Condensates are often seen in the cooler portion of the apparatus and their contribution to gas evolution depends on the vapor pressure of the liquid. Volatile reactants and products are removed from the reaction zone to the cooler parts of the apparatus. In compatibility testing, samples may contain up to 50 percent of a deliberately added, inert component. This percentage may be grossly in excess of what the explosive will encounter in practice.

All of the methods summarized above have some validity given their known limitations, but surprisingly enough, the very simple vacuum stability technique persists and shows no sign of being completely replaced. Indeed, under the auspices of NATO, consideration is being given to the development of a standard vacuum stability test.

In the standard Navy test, an explosive plus an additive are considered to be incompatible if the gas volume evolved by the mixture is greater than the sum of the gas volumes from separate tests on the explosive and additive. This standard seems somewhat arbitrary since the criteria for the vacuum stability of explosives permits the evolution of up to two milliliters of gas before the explosive is considered unstable. This situation arises because it is not known how much instability can be tolerated safely in an explosive system.

The standard stability/compatibility criteria are designed to insure the safe storage of explosives for long periods. Based on the storage history of standard explosives, small changes in decomposition rates may not be significant, even during storage periods of 10 or 20 years. It may not be reasonable to apply the same incompatibility criteria to a polymer system which may contact the components of an explosive train for a limited time period. An unrealistic set of criteria will only increase the difficulty of finding a usable polymer composition.

2.4 MATERIAL SELECTION

The selection of thermosetting polymeric materials which can be cured in contact with a variety of explosives and energetic materials requires that all facets of the polymers' physical properties and the polymer explosive interaction be considered.

2.4.1 Compatibility

The plastics and explosives literature has

been briefly surveyed in an effort to lay a basis for the future development of a polymer system suitable for defense requirements. Since most, if not all, fuze train and booster explosives are incompatible with basic materials and alkalis, it follows that a compatible system must be chemically neutral or somewhat acidic. Fuze train and booster explosives, with the possible exception of lead azide, are probably compatible with weakly acidic materials at temperatures up to about 50°C.

2.4.2 Viscosity

Most thermosetting polymer compositions that are free-flowing liquids in the uncured state at room temperature will either become viscous or solidify at temperatures as low as 10°C. Reactive or nonreactive diluents can be added to reduce the viscosity of these systems for deployment at low temperatures. However, these additives will reduce the reactivity and increase gel times.

2.4.3 Gel Time

For every 10°C change in temperature, the rate of a chemical reaction will approximately double or be decreased by one-half. Thus, a polymer system that gels in 3 minutes at 25°C will not gel for a long time at -10°C. Conversely, a polymer system that gels rapidly at -10°C will react violently at 25°C. By packaging the system so that variable amounts of catalyst can be added to the polymer, adjustments in the gel time as a function of temperature can be made.

2.4.4 Exotherm

The heat of the polymerization reaction, if liberated in a short time, will result in substantial increases in the temperature of the reacting polymer. With some acid-curing epoxy systems, peak exotherms may reach 250°C or higher without external heating, and this is above the decomposition temperature of most explosives. As a practical matter, the peak exotherm depends on the mass of the system and the rate at which heat can be dissipated. Peak exotherms depend also on the type of polymer system and the curing agents and catalysts used. Given the high thermal conductivity of items containing large amounts of metal, high exotherms may not be a serious problem.

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5. BIOGRAPHY

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Mr. Heller joined the Naval Surface Weapons Center in 1955 as a Research Chemist with the responsibility for conducting advanced research on new explosive compositions. He is responsible for the development of three new explosive compositions in current use by the U. S. Navy, and a new explosive composition used by NASA in the Apollo program.