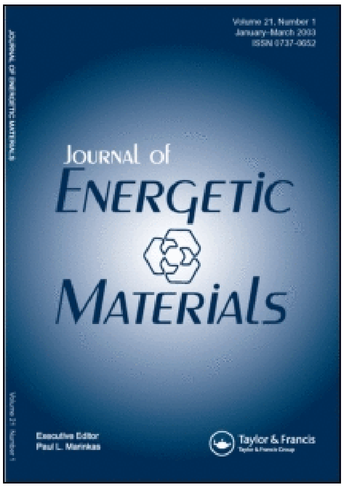

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RADIATION CURE OF EXPLOSIVE/PROPELLANT FORMULATIONS

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ABSTRACT

The feasibility of radiation curing energetic compositions has been demonstrated. Binders consisting of vinyl-terminated polybutadiene-acrylonitrile copolymer (VTBN) and a combination of styrene and 2-hydroxyethyl methacrylate have been cured using x-rays at a dose of 1.2 x 10^6 roentgen to give flexible, rubbery solid materials with rupture stress of 0.8 to 8.3 MPa and strain of 130-230 percent at 25°C.

Irradiation of RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane) at the 1.2 x 10^6 roentgen dose level caused no measurable nitramine decomposition.

The VTBN binder system loaded with 70% nitramine energetic filler was cured by irradiation (1.2 x 10^6 roentgen) to give rubbery solids with 2.2 - 2.8 MPa stress at rupture and nearly 100% strain (25°C). The filled systems display Taliani slopes, nitramine phase transitions and decomposition temperatures which are well within normal limits for explosives and propellants.

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INTRODUCTION

Many present-day energetic formulations contain finely ground explosives or oxidizers dispersed in polymeric fuel binders. The binders are typically cured by catalyzed thermal reactions; i.e., chemical curing agents are incorporated into the mix and the energetic material is thermally cured in hot air ovens. Inherent in the processing procedure is the "pot-life" restriction brought about by a continually curing system. For example, a typical propellant or explosive pot-life is 4 to 6 hours at 60°C; all mixing, handling, and loading must be accomplished within that fixed time period.

For efficient large-scale production of energetic materials, it would be desirable to have a method which combines an indefinite pot-life for the material mix and an ambient temperature instant cure procedure. Neither of these options is available with current technology, but could be provided by a radiation curing process. Since no chemical catalysts are used, the pot-life of a mix prior to irradiation is indefinite and the mixing viscosity remains constant. A radiation-induced cure requires much less time than the conventional catalyzed thermal cure (which usually takes 3 to 7 days). Suitable sources of ionizing radiation include x-rays and electron beams.

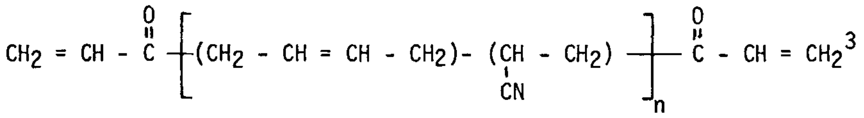
The net effect of ionizing radiation on most organic compounds is the production of free radicals. To be susceptible to cure by irradiation, the polymeric binder must possess chemical groups which respond efficiently to free-radical initiated reactions. A vinyl-terminated polymer, for example, introduces the necessary groups into the binder system to bring about chemical crosslinking when subjected to ionizing radiation. The vinyl end groups can also be incorporated into a rapidly homopolymerizing unsaturated monomer which is sensitive to ionizing radiation.

A survey of published literature on polymeric systems indicates that radiation cure of polymers is feasible. For example, unsaturated urethanes[1] have been polymerized via gamma-irradiation at doses of 10^6 to 10^7 roentgen (R); unsaturated polyester-styrene systems[2] have been copolymerized with 10^6 to 10^7 rad electron dose.

This paper describes the development of a method for curing unsaturated polymeric binder/nitramine energetic compositions via x-ray irradiation.

BINDER FORMULATION

Vinyl-terminated polybutadiene-acrylonitrile copolymer (VTBN, manufactured by the B. F. Goodrich Chemical Company) was chosen as the prepolymer component of the binder system under development. VTBN is a low molecular weight linear liquid polymer with reactive terminal vinyl groups. The structure for this polymer is:



$$CH_2 = CH - \overset{O}{\overset{\|}{C}} \left[(CH_2 - CH = CH - CH_2) - (\underset{CN}{\underset{|}{CH}} - CH_2) \right]_n \overset{O}{\overset{\|}{C}} - CH = CH_2$$ [3]

VTBN is cured to a solid elastomeric mass via a free-radical mechanism. Though the polymer can be homopolymerized, it is desirable to copolymerize VTBN with unsaturated monomers of low viscosity in order to improve processability and to improve mechanical properties by separating VTBN molecules with linear monomer units[3].

Two VTBN prepolymers have been compared in binder studies. The 16.5% acrylonitrile content polymer (VTBN A) is a commercial product and the 10.0% acrylonitrile content polymer (VTBN B) is an experimental material custom-made for this program. Characterization data for the polymers are presented in Table 1.

TABLE 1. Properties of VTBN Polymers

Property	VTBN 1300 X 22 (VTBN A)	VTBN Experimental (VTBN B)
Acrylonitrile Content, %	16.5	10.0
Viscosity at 27^{o}C, Poise	2000	648
Vinyl Equivalent Weight	1316	1341
Specific Gravity at 25^{o}C/25^{o}C	0.984	0.945

Four monomers were evaluated in gumstocks with the VTBN polymers in orde to determine which when cured gave binder systems having the best mechanical properties. The monomers tested were: styrene, methyl methacrylate, 2-hydroxyethyl methacrylate, and hexanediol diacrylate.

Gumstocks of VTBN with styrene or methyl methacrylate had little physical strength; those with hexanediol diacrylate as the monomer were brittle and shattered when samples for physical property measurements were cut. It was originally thought that binders made with diacrylate would have better mechanical properties than those made with monoacrylates due to chain extension reactions. Instead, the opposite proved to be true. The explanation was traced to the fact that the VTBN polymer as received from B. F. Goodrich Chemical Company contains a small amount of diacrylate residue from the polymer synthesis and that the prepolymer has an effective random functionality much higher than two.

From the preliminary screening of polymer-monomer combinations, only those containing VTBN and a combination of styrene and 2-hydroxyethyl methacrylate were found to be flexible as well as tough. Formulations selected for irradiation were:

VTBN/styrene/2-hydroxyethyl methacrylate
6/6/3 (wt ratio)
6/7/2 (wt ratio)

Binders were made with both 10 and 16.5% acrylonitrile content VTBN polymers in order to compare physical properties. Binder gumstocks were prepared by mixing the polymer with the monomers; the gumstocks were poured into Teflon-coated aluminum molds (approximately 1mm deep and 65mm in diameter) and degassed for one hour at ambient temperature and vacuum (4mm Hg) in order to remove air bubbles. The molds were sealed with polyethylene plates. The binders were subjected to two x-ray dose levels, 1.0 and 1.2 x 10^6 roentgen (R), provided by a General Electric 2000 KVP x-ray unit. Formulation and mechanical property data for the irradiated binders are listed in Table 2.

TABLE 2. Formulation and Mechanical Property[1] Data For Irradiated Binders

Formulation[2], weight %				X-Ray Dose[3] R X 10^6	Stress MPa	Strain %
VTBN A	VTBN B	Styrene	HEMA			
40	0	40	20	1.0	7.6	170
				1.2	8.3	220
0	40	40	20	1.0	4.1	170
				1.2	4.5	160
40	0	46.7	13.3	1.0	3.2	220
				1.2	5.2	230
0	40	46.7	13.3	1.0	0.76	130
				1.2	0.96	160

[1] Micro-dogbones (5.6 mm^2 cross-sectional area) were pulled at a strain rate of 5.1 cm per minute using a Scott Model X5 Tester. Measurements were made at 25°C.

[2] VTBN A: VTBN, 16.5% acrylonitrile
VTBN B: VTBN, 10% acrylonitrile
HEMA: 2-Hydroxyethyl methacrylate

[3] R: Roentgen

The irradiated binders cured to flexible solids; they did not break or crack when bent 180^o. A more complete cure was obtained at the higher dose level. Because the VTBN A (16.5% acrylonitrile)/styrene/2-hydroxyethyl methacrylate binder (6:6:3 weight ratio) displayed the highest combination of elongation and tensile strength values of those irradiated, it was selected as the system to be filled with 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and with 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX).

EVALUATION OF RADIATION DAMAGE TO NITRAMINES

Pure samples of RDX and HMX were irradiated at the same dose as the gumstocks to determine their radiation stability and the safety characteristics of the process. The nitramines, of approximately 200 micrometer particle size, were placed in gumstock molds and irradiated at a dose of 1.2×10^6 R. There were no indications of any safety problems with the irradiation of these energetic materials. The irradiated samples were evaluated for changes in thermal stability using the nitrogen Taliani Test and Differential Scanning Calorimetry (DSC).

In the Taliani test, 1.0 gram samples of materials are heated in a nitrogen atmosphere at 110^oC in a closed system at constant volume and in contact with the gaseous decomposition products (if any). The nitrogen is at atmospheric pressure at the beginning of the test. As the sample is heated, the pressure increase is measured. The relative stability of different samples is correlated by comparing pressure-time slopes; slopes greater than 1.0 mm/minute indicate incompatibility within the sample and insufficient thermal stability. Slopes of approximately 0.1 mm/minute are typical for composite propellant compositions.

The Taliani test results for irradiated and non-irradiated ("control") HMX and RDX samples are presented in Table 3. They show that the pressure-time slope values for control and irradiated nitramines are virtually identical, indicating little if any degradation due to irradiation. RDX was observed to be slightly less stable than HMX.

TABLE 3. Taliani and DSC Results for Nitramines and Nitramine-Filled Binders

Material	Slope[1] (mm/min)	DSC (°C)[2]		
		T_M	T_D	T_P
Control RDX	0.04	204-210	210-240	-
Irradiated RDX	0.06	204-210	210-240	-
Irradiated RDX-Binder	0.18	-	208-220	-
Control HMX	0.02	-	278-288	187
Irradiated HMX	0.03	-	278-285	182
Irradiated HMX-Binder	0.03	-	243-255	185

[1] Nitrogen Taliani pressure-time slopes

[2] T_M - Melting peak temperature

T_D - Decomposition peak temperature

T_P - Phase transition peak temperature

DSC studies were conducted on small samples (3 mg) of nitramine in a nitrogen atmosphere at a heating rate of 5°C/minute using a DuPont 990 Thermal Analyzer with DSC module. The temperature difference between the material under investigation and the thermally inert reference sample (sealed aluminum pan with pin hole) was measured. Phase transition, melting, and decomposition temperatures of the nitramines are presented in Table 3. No measurable decomposition of the nitramines appears to have occurred upon irradiation.

EVALUATION OF NITRAMINE-FILLED BINDERS

Two one-hundred gram mixes were made in the Baker-Perkins high-shear one-half pint mixer at the 70% solids loading level with a 70:30 A:E (approximately 200 micrometer and 20 micrometer particle size, respectively) blend of nitramine in the VTBN binder. The RDX mix was fluid and therefore processed and cast well; the HMX-filled system was not as fluid but was still castable. This suggests that some RDX is dissolving in the binder. The HMX-filled binder system should have been less viscous than the corresponding RDX composition based on the lower volume loading. All mixing was carried out at ambient temperature and atmospheric pressure; no degassing step was included. The mixes were cast into the previously used gumstock molds, sealed with polyethylene lids, and irradiated at the 1.2 x 10^6 R dose level.

The filled binders cured to rubbery solids. Microdogbones (12.1 mm^2 cross section) were cut from the cured material and tested for mechanical properties at 25^oC. The RDX-filled system has a stress of 2.2 MPa and a strain of 70%. The stress of the HMX-filled binder was measured at 2.8 MPa and its strain as 100%.

Taliani data for the irradiated filled binders is presented in Table 3. The gassing rates for both the HMX and RDX compositions are well within the acceptable limit of less than 1.0 mm/minute. The slope for the HMX-filled binder is unchanged from that of the nitramine alone. While the slope for the binder loaded with RDX is higher than that for RDX alone, it is only slightly higher than the typical Taliani slope of 0.1 mm/minute for composite propellants.

DSC and Thermal Mechanical Analysis were carried out on the irradiated nitramine-filled binders in order to determine decomposition and glass transition temperatures, respectively. Decomposition temperatures of RDX and HMX (see Table 3) are lowered slightly when used in combination with the binder system, indicating that some chemical interaction occurs. Phase transition temperatures for neat HMX and HMX in combination with the binder system are virtually identical. The DSC results for the irradiated nitramine loaded binders are consistent and well within normal limits for neat nitramines and existing nitramine propellant and explosive systems. Glass transition temperatures were observed to be -48 and -50°C for the RDX and HMX-filled binder systems, respectively.

CONCLUSIONS

The feasibility of radiation curing VTBN with unsaturated monomers has been demonstrated. Binders consisting of VTBN and a combination of styrene and 2-hydroxyethyl methacrylate have been cured using x-rays at a dose level of 1.2×10^6 roentgen to give flexible, rubbery solid materials with 0.8 to 8.3 MPa stress and 130 to 230 percent strain at 25°C.

Irradiation of pure RDX and HMX at the 1.2×10^6 roentgen dose level caused no measurable nitramine decomposition.

The VTBN binder system filled with 70% nitramine energetic filler cured via x-ray irradiation (1.2×10^6 roentgen) to give rubbery solids having rupture stress of 2.2 to 2.8 MPa and strain of nearly 100% at 25°C. The filled systems display Taliani slopes and nitramine phase transition decompositi temperatures which are well within normal limits for composite propellants and explosives.

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