New Directions in the Area of Modern Energetic Polymers: An Overview

D. M. Badgujar[a], M. B. Talawar[b],
V. E. Zarko[c], and P. P. Mahulikar[a]

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Abstract: Energetic polymers containing nitro, nitrato, and azido groups release high energy during combustion and thereby increase the performance of the systems. A number of energetic polymers have been found suitable for use as binders in high-performance propellant and explosive formulations. This review describes the synthetic and application aspects of various modern energetic polymers for explosive formulations and propellants.

Keywords: energetic polymers, thermoplastic elastomers, energetic binders, plastic bonded explosives (PBX), energetic plasticizers, carborane polymers, energetic polyphosphazenes.

INTRODUCTION

Energetic polymers are compounds that generally contain energetic groups (explosophores) such as the nitro-, nitrato-, azido-, etc., and their combustion products contain a significant amount of nitrogen gas. Energetic polymers are of interest for use as binders in propellants and explosives [1]. The binders can be specially synthesized polymers containing explosophores or ordinary polymers in combination with energetic plasticizers, namely, nitroesters, nitramines, and nitro- and azido-compounds. The use of these binders is aimed at developing high-energy, smokeless, explosion-proof and low-vulnerability composite energetic systems.

Energetic polymers are usually obtained by polymerizing energetic monomers, e.g., polyNIMMO from 3-nitratomethyl-3-methyloxetane (NIMMO) [2, 3] and poly-GLYN from 2-nitratomethyloxirane (GLYN) [4, 5] or by introducing energetic groups into existing poly-

mers, as, e.g., in the manufacture of nitrocellulose from cellulose [6], picryl nitrocellulose from cellulose [7], polyvinyl nitrate from polyvinyl alcohol [8] and nitrated polybutadiene from polybutadiene [9].

1. ENERGETIC POLYMERS AND PREPOLYMERS

Energetic polymers (Table 1) can be used in the production of low hazard, high power explosives, thus providing reduced solid loading without loss of power. The main problem is to obtain practically acceptable polymers with proper energy density.

A number of energetic polymers containing nitrate ester functionality have received attention for use as binders in high performance propellant and explosive formulations. Nitrated hydroxyterminated polybutadiene (NHTPB) [10] is synthesized by epoxidation of the double bonds of HTPB oligomers with peroxyacetic acid [11], followed by ring-opening nitration of the resulting epoxide functionality with dinitrogen pentoxide in methylene chloride [12]. Nitrated HTPB with 10% double bonds is a usable prepolymer with a viscosity significantly low enough to permit easy processing and high solids loading. Such prepolymers can be cured

[a]School of Chemical Sciences, North Maharashtra
University, Jalgaon, 425001 India;
mahulikarpp@rediffmail.com.
[b]High Energy Materials Research Laboratory,
Pune, 411021 India.
[b]Voevodsky Institute of Chemical Kinetics and Combustion,
Siberian Branch, Russian Academy of Sciences
Novosibirsk, 630090 Russia; zarko@kinetics.nsc.ru.

Table 1. Structures of energetic polymers [1]

Common name	Chemical name	Structure
NHTPB	Nitrated HTPB	
NIMMO (monomer)	3-Nitratomethyl-3-methyl oxetane	
PolyNIMMO	Poly(3-nitratomethyl-3-methyl oxetane)	
GLYN (monomer)	Glycidyl nitrate	
PolyGLYN	Poly(glycidyl nitrate)	
GAP	Glycidyl azide polymer	
AMMO (monomer)	3-Azidomethyl-3-methyl oxetane	
PolyAMMO	Poly(3-azidomethyl-3-methyl oxetane)	
BAMO (monomer)	3, 3-Bis-azidomethyl oxetane	
PolyBAMO	Poly(3,3-bis-azidomethyl oxetane)	

with aliphatic or aromatic diisocyanates to give energetic binders.

NIMMO [13] is synthesized by selective nitration of the hydroxy group of 3-hydroxymethyl-3-methyloxetane with dinitrogen pentoxide in an inert solvent. The cationic polymerization of NIMMO using an initiator system of boron trifluoride and diol yields the energetic polymer polyNIMMO [14]. PolyNIMMO generated by this process is a viscous liquid with a very low sensitivity to impact and well suited for use as an energetic binder for rocket propellants and plastic bonded explosives (PBXs).

Glycidyl nitrate (GLYN) is synthesized [15] in high yield and purity by selective nitration of glycidol with dinitrogen pentoxide in an inert solvent. The cationic polymerization of glycidyl nitrate is more difficult than

the polymerization of NIMMO and requires a strong mineral acid such as tetrafluoroboric acid. The product, polyGLYN [16], is a low-molecular-weight hydroxy-terminated prepolymer which reacts with diisocyanates to give energetic polyurethane polymers [17]. Millar and co-workers [18] have reported on an improved process for producing poly GLYN which is well suited for use as an oligomer in solid high-energy compositions.

Millar and co-workers [19] have also described the use of low-molecular-weight polyGLYN as an energetic plasticizer. In this context, polyGLYN has a number of advantages over traditional nitrate ester plasticizers, including: low volatility, low glass transition temperature ($-40°$C), excellent miscibility with the binder and decreased plasticizer mobility. On the basis of performance and the ease with which polyGLYN is prepared via dinitrogen pentoxide technology, it seems likely that it will prove to be a world leader in the field of energetic polymers. It has been shown [20] that propellants with polyGLYN and polyNIMMO binders have a higher specific impulse than modified composite double-base systems ($\approx$260 s).

Recent interest has turned to nitrated cyclodextrin polymers (polyCDN) for potential use in insensitive and minimum smoke producing propellants [21]. The synthesis, purification and characterization of the following polymers has been studied in detail [22]:

(1) r-cyclodextrin polymer cross-linked with 1-chloro-2,3-epoxypropane,

(2) r-cyclodextrin polymer polymer cross-linked with 4,4-methylene-bis (phenyl isocyanate).

Prominent among the energetic groups is the azido group [23], which has a heat of decomposition of $\approx$355 kJ per one N_3 group. The feasibility of using low-molecular-weight azido compounds such as 1,7-diazido-2,4,6-trinitrazaheptane and 1,3-diazido-2-nitrazapropane in solid propellants has widened the scope of application of azide compounds beyond the class of initiators [24]. It was logical to extend the scope of azide containing molecules further to the area of polymers. The first polymer to be developed in this category was glycidyl azide polymer (GAP), which came into prominence during the early 1990s. Subsequently, a series of poly azido oxetanes emerged on the scenario [25].

Azido polymers, particularly glycidyl azide polymer (GAP) [26] and co-polymers of bisazidomethyloxetane (BAMO) [27], have entered the domain of advanced propulsion systems. Poly 3-nitrato methyl-3-methyloxetane (PNIMMO) [28] and poly glycidyl nitrate (PGN) [29] have also made foray in the area of advanced systems. BAMO and nitrato methyl methyloxetane (NIMMO) copolymer are fast emerging as energetic thermoplastic elastomers for wide applications

in the area of extruded composite rocket propellants as well as pressed/sheet explosives [30].

Prepolymers are used in energetic formulations such as cast cured explosives and propellants to give mechanical resistance, to increase the stability to impact, friction and heat, as well as to provide encapsulation of crystalline energetic crystals. Energetic prepolymers also contribute to the amount of released energy. Due to its good performance [31], GAP is a widely used prepolymer that contains azido groups. Poly (3-azidomethyl-3-methyl oxetane) (PAMMO) and poly(3,3-bis-azidomethyl oxetane) (PBAMO) are other prepolymers with azido groups [32, 33]. Heterocyclic compounds have higher predicted thermal and shock stability and density than carboxylic compounds [34]. The higher nitrogen content also leads to lower oxygen requirements in energetic formulations [35]. Under conditions of high temperature and pressure, it gives polycyclic systems, which are known to be burning rate modifiers [36]. The compound 2-oxy-4,6-dinitramine-s-triazine (DNAM) significantly increases the burning rate of PSAN/HTPB formulations, maintaining good shock stability properties [37]. The energetic prepolymers containing the 1,3,5-s-tritriazine ring and azido groups in their structure were synthesized by the reaction of inert precursors with sodium azide.

1.1. Melamine/Epichlorohydrin Based Prepolymers

The reaction of melamine with ethylene oxide or glycidol (2,3-epoxy-1-propanol) was patented in 1945 [38]. The basic catalysts NaOH, KOH, Ca(OH)$_2$ or pyridine were used. Subsequently, polyol with at least two hydroxyl groups was used to produce similar compounds. Sodium and potassium methoxides were also used as catalysts at temperatures of 150–200°C. Kucharski et al. [40] studied the reaction between melamine and ethylene oxide or propylene oxide (PO) in N,N-dimethylformamide (DMF), using tetrabutylammonium hydroxide (TBAH) as catalyst. Lubczak et al. [41] used dimethyl sulfoxide (DMSO) as solvent. Mixtures of different products were found, revealing unequal side branches of the triazine ring. It is well known that melamine derivatives also react with oxiranes via anionic polymerization, with the catalyst TBAH [42, 43], triethylamine, KOH, NaOH, sodium methoxide and potassium ethoxide [44–49]. DMSO, DMF, and water were used as solvents. All the melamine derivatives contained hydroxyl end groups, formed by the reaction of melamine with acetyl groups or formaldehyde. In most cases, ethylene and propylene oxides or epichlorohydrin (ECH) were used.

Table 2. Energy performance of pseudo-propellants containing modern high-energy materials [30]

Propellant formulation (binder/plasticizer/oxidizer/fuel)	I, s	I_V, s·g/cm^3
HTPB/AP/Al	264.5	464
GAP/AP/Al	255	492
GAP/AN/Al	261.5	463
GAP/AN/CL-20/Al	263.7	475
GAP/ CL-20/Al	273	521
GAP/ADN/Al	274.2	491
GAP/HNF/Al	272.6	492
GAP/TMETN/BTTN/RDX (63%)	283.5	405
GAP/TMETN/BTTN/RDX (60%)	242	411
GAP/TMETN/BTTN/CL-20 (63%)	252	452

Here I is the specific impulse and I_V is the volume specific impulse.

1.2. Energetic Polymers and Their Salts

Energetic polymers from azoles have good compatibility with the solid propellant ingredients and are thermodynamically stable and relatively safe in handling [50–54]. The preparation poly(N-vinyl-imidazolium) salts as highly ion-conductive polymer electrolytes is reported in [55]. Energetic materials that are salts often have lower vapor pressure and higher densities than their atomically similar nonionic analogues. In these ionic species, the cation is generally an organic ion with low symmetry.

Heterocyclic nitrogen based salts are widely used along with energetic compounds containing inorganic anions such as nitrate, perchlorate, azide, nitrocyanomethanide, nitroformate, or dinitramide [56] or energetic organic anions such as picrate, imidazolate, triazolate, and tetrazolate [57]. Five-membered nitrogen-containing heterocycles are excellent precursors to energetic materials. The polymerization of N-vinyl-1, 2, 4-triazolium monomers or the protonation of poly(1-vinyl-1,2,4-triazole) lead to the formation of salts with anions such as nitrate, perchlorate, picrate, or azolate, for example, 4,5-dinitro-imidazolate, 3,5-dinitro-1,2,4-triazolate, or 5-nitrotetrazolate. Shreev et al [58] reported the synthesis of energetic polymer salts from 1-vinyl-1,2,4-triazole derivatives via free radical polymerization of 1-vinyl-1,2,4-triazolium monomer salts or by protonation of poly(1-vinyl-1,2,4-triazole) by inorganic or organic acids.

2. ENERGETIC BINDERS

Energetic binders contain high-energy functional groups (explosophores), mostly, the nitro (—C—NO$_2$), nitramino (—N—NO$_2$), difluoroamino (—NF$_2$), azido (—N$_3$), and nitrate ester (—ONO$_2$) groups. A number of papers report on the synthesis procedures and properties of promising azido polymers such as GAP [59, 60], PBAMO [61], and polymers with nitrate groups, namely, polyGLYN and NIMMO [62].

Energetic binders are of growing importance in the formulation of cast-cured composite solid propellants. They are, in the majority of the cases, low-molecular-weight hydroxyl-terminated polyethers with azido or nitro groups. Usually, in the propellant mixture, a hydroxyl-terminated low-molecular-weight polymer reacts with isocyanates to form a cross-linked polyurethane matrix that binds together the solid propellant components in a tough elastomeric three-dimensional structure. These binders can increase the burning rate and specific impulse in propellant systems based on ammonium nitrate, perchlorate, and dinitramide and nitramines due to their high heat of formation and the capability of evolving gaseous decomposition products. Additionally, oxidizers such as ammonium perchlorate can be replaced by halogen-free compounds to get propellants with low signature. Data on the energy performance of GAP based pseudo-propellants are given in Table 2.

Energetic binders are polymers which crosslink explosive ingredients together with a plasticizer into a tough yet flexible three-dimensional network. Plasti-

Table 3. Physicochemical properties of energetic binders [66]

Binder	ΔH_f, kJ/mol	ρ, g/cm^3	T_{gl}, °C	OB, %
GAP	+117	1.30	−121	−45
PBAMO	+413	1.30	−124	−45
PAMMO	+179	1.06	−170	−35
PolyNIMMO	−335	1.26	−114	−25
PolyGLYN	−285	1.39	−61	−35
HTPB	−52	0.92	−324	−65
BAMO–THF	+189	1.18	−125	−56

Here THF is tetrahydrofuran, ΔH_f is the heat of formation, ρ is the density, T_{gl} is the glass transition temperature, and OB is the oxygen balance.

cizers are typically added both to facilitate processing and to improve the mechanical properties of the final cured formulation. The emergence of novel propellants having a unique combination of high energy and low vulnerability became possible due to the development of energetic polymers. Prepolymers having exothermically decomposing azido groups or oxygen-rich nitro and nitrato groups offer formulations with a superior performance potential at relatively low solid loading.

The use of energetic binders in the production of explosives with polymer binder (PBX) provide an increase in energy output, along with lower vulnerability and potential environmental benefits. For example, incorporation of degradable functionalities in the polymer backbone of energetic binders allows for the recovery and possible reuse of munitions [62]. In addition, it is expected that these new energetic binders will lend themselves well to insensitive munitions, where a lowering of vulnerability with incorporation of an energetic binder occurs.

There is an extensive bibliography on common in-service energetic binders [53, 63–65]. A new energetic polymer — poly(2-nitratoethyloxirane) (polyNEO) — has been recently reported [66]. These polymers owe their energetic properties to the presence of one nitrato group (polyNIMMO, polyGLYN, and polyNEO) or one or two azido groups (GAP, polyAMMO, and polyBAMO) per monomer unit. Data on the physicochemical properties of binders are given in Table 3.

In the last twenty years, azido polymers have gained interest in the field of energetic binders for solid rocket propellants. For such application, a polymer should possess the following properties: amorphous character and low glass transition temperature, presence of hydroxylic end groups (to allow the formation of a polyurethane network after in situ curing with iso-

cyanates), controlled molecular weight, and low final polydispersity. The basic idea is to substitute the actually used polybutadiene with something that could act not only as a binder but also as a real propellant component. In this respect, a valid solution is the insertion of azido groups due to their tendency to exothermally decompose with nitrogen evolution. There are two possible synthetic strategies for the preparation of energetic azido polymers: (1) homo- or copolymerization of etheric monomers containing the azido group in the side chains; (2) synthesis of a polyether with suitable groups (i.e., halogen atoms) in the side chain and subsequent introduction of azido groups by nucleophilic substitution.

An effective method for the synthesis of GAP has recently been proposed by Kshirsagar et al [67]. It has been shown that exposure to microwave radiation for a short time (10 min) leads to conversion of CH_2—Cl to CH_2—N_3. PECH-Triol (polychlorohydrin) was used as a precursor with the formation of the end product GAP-Triol.

2.1. Energetic Thermoplastic Elastomers As Binders

Thermoplastic elastomers (TPE) containing hard and soft segments are emerging as high potential binders for advanced propellants and explosives. TPE form reversible curable systems, unlike isocyantes cured ones. This occurs when the binder (polymer matrix) for explosives and propellant systems based on irreversible cross-linked thermoset polymers is transformed to reversible, physically cross-linked thermoplastic elastomers [68]. A TPE polymer would enable the recovery and reuse of the ingredients of a system and could lower the life cycle wastes. Upon melting, the ingredients bound together in the TPE can be separated, recovered, and saved for future use. This results in cost savings and environment friendly demilitarization and disposal. To facilitate this, TPE polymers that melt/soften at a safe processing temperature range of 85–100°C are desirable [69].

Typically, such polymers contain hard (crystalline) blocks and soft (non-crystalline) blocks. They have reversible spherulitic crosslinks (polymers crystallized from melt show circular birefringent regions called spherulites). These crosslinks disappear above the melting point of the crystalline hard blocks. The physical crosslinks reform upon cooling. Non-energetic TPEs include Estane, Hytrel, EVA and Kraton; energetic thermoplastic elastomers include BAMO–AMMO and BAMO–NIMMO copolymers and GAP based TPEs.

An attempt to synthesize an energetic polymer by copolymerization of glycidyl azide monomer with BAMO monomer was undertaken by Keicher et al [70].

Table 4. Performance of propellants based on BAMO–AMMO polymers [71]

Composition	F, J/g	ρ, g/cm^3	T_f, K
M30	1081	1.674	3006
24% BAMO–AMMO, 24% TAGN, 52% CL-20	1166	1.65	2794
24% BAMO–AMMO, 24% TAGN, 52% RDX	1089	1.57	2493

Here M30 is nitroguanidine/ammonium nitrate/ethyl centralite, TAGN is triaminoguanidine, CL-20 is isowurtzitane, F is the force of the propellant, ρ is the density, and T_f is the flame temperature.

It was assumed that the introduction of BAMO blocks into the GAP chain would lead to an increase in the amount of nitrogen atoms compared to their initial content in GAP (42.4%) and to a corresponding increase in the energy content. Unfortunately, it was found that the nitrogen content in the copolymerized polymer was reduced (35.1%) due to the introduction of CH_2CH_2O from dioxane solvent into the polymer matrix. At the same time, the synthesized polymer has lower impact sensitivity, lower glass transition temperature, and a reduced content of cyclic oligomers. The polymer has been successfully tested in an aluminized solid propellant based on ammonium perchlorate, and efforts are underway to improve its synthesis for the purpose of increasing its nitrogen content.

The energy performance of propellants based on BAMO–AMMO thermoplastic elastomers are given in Table 4 in comparison with the three-base M30 gun propellant.

TPE binder was recovered [71] almost totally with only 19.42 ppm of the solid oxidizer as a contaminant, and with little or no change in the number average molecular weight or weight average molecular weight of the BAMO–AMMO copolymer. The ammonium perchlorate removal process was done first to reduce the hazards associated with the energetic binder filled with oxidizer. Likewise, a TPE based gun propellant was separated by non-chlorinated solvent process to recover 99% of the nitramine and 98% of the binder. Similarly, a TPE based high explosive composition ingredients were separated with 99% recovery of pure CL-20 and 95% recovery of the binder.

TPE energetic formulations do not always have to be separated into various components in order to be reused. Under the Electrothermal-Chemical (ET) gun propellant program, for example, three hundred pounds of seven-perforation gun propellant were remelted and formed into rolled sheet propellant without removing

or adding any components to the original formulations. No change in laboratory safety characteristics, propellant density, or mechanical properties was observed as a result of the re-processing. The burn rate decreased slightly during the first three cycles and then increased approximately 3% higher than the average for the first three iterations. A flow diagram for the recycle of TPE based rocket propellant is given in the figure.

The use of energetic thermoplastic elastomers eliminates the need for chemical cross-linking agents, makes processing easier due to their low melt viscosities, and eliminates the need for solvents during casting. Their superior processing qualities and the ease of demilitarization and recycling make these materials a much more environmentally sound choice for energetic binders. However, their synthesis still involves the use of large quantities of toxic chemicals, such as methylene chloride, as solvents.
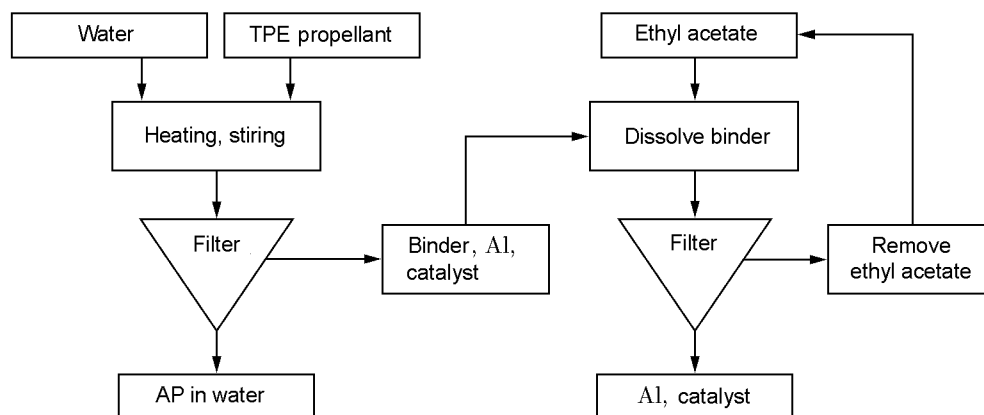
2.2. Polymer Bonded Explosives

During the manufacture of munitions, a crystalline high-energy filler is usually embedded in a polymer matrix in order to reduce the sensitivity of the former toward accidental initiation. This stratagem, coupled with the use of new, less heat- and impact-sensitive explosives [72–74] aims to develop and augment a whole new class of safer weapons, which are generally described as insensitive munitions (IM) [75, 76]. The first polymer bonded explosive (PBX), consisting of a composition of RDX crystals embedded in plasticized polystyrene [77], was developed in 1952 at Los Alamos Scientific Laboratories in the US. A variety of PBX formulations based on an inert polymer matrix, such as urethane cross-linked hydroxyl terminated polybutadiene (HTPB) [78–80], were subsequently developed. The loss of explosive performance caused by the presence of the relatively low-density inert polymer binder, however, soon led to the development of novel polymers which were themselves energetic and thus, could actively contribute to the explosive performance of the PBXs.

HMX-based PBXs were developed for projectiles and lunar seismic experiments during the 1960s and early 1970s using Teflon (polytetrafluoroethylene) as the binder. PBXs based on RDX and RDX/PETN (known as Semtex) [81] have also been developed. Development is continuing in this area to produce new PBXs containing energetic polymers that will contribute to the explosive performance.

2.3. Energetic Carborane Polymers

When one considers the potential high-energy release on rupture of a carborane unit, together with the

Flow diagram of separation and recovery methods of ingredients in TPE propellants.

Table 5. Enthalpy of formation of o-carborane and its combustion products [83]

Compound	ΔH_f, kJ/mol
o-$C_2B_{10}H_{12}$ (s)	-170
BO (g)	$+25.0$
BO_2	-300.4
B_2O_3	-843.8
H_2O (g)	-241.8
CO (g)	-110.5
CO_2 (g)	-393.5

thermodynamic stability of combustion products, it is hardly surprising that there is a body of literature that reports on the use of carboranes within formulations. Their use in energetic applications is to be expected when the enthalpy of formation (ΔH_f) data for the products of combustion for boron are compared to those of carbon. Thermodynamic data for the enthalpy of formation of o-carborane and typical boron and carbon combustion products are shown in Table 5.

Vinyl- and allylcarborane containing polymers and copolymers [82, 83] have been used as solid propellant binders. The incorporation of oxidizers, for example, NH_4ClO_4, $KClO_4$ or NH_4NO_3, makes high-impulse propellants having high burning rate and high heat of combustion. The mechanical strength and burning characteristics of the propellant can be greatly altered by the addition of a resin based on either urea- or phenol-formaldehydes. Composite propellants with burning rates in the range of 4–20 mm/s are formed when carborane burn rate modifiers, for example, alkyl-carboranes, geminal NF carboranes, and siloxy- or silyl-carboranes, are incorporated into the formulation. Burn

rates up to 400% (when compared to a control propellant) are obtained for 10–14% (by weight) ballistic modifier. In the literature, there are reports of carborane units bearing energetic groups, including nitro- and nitro-phenyl. The treatment of o-carborane with 100% nitric acid at room temperature is reported in [84] to yield B-hydroxyl-o-caborane and B-nitrato-o-carborane. The nitrate compound was reported as being extremely unstable and detonated on heating, presumably due in part to the electron-withdrawing nature of the carborane. However, the reaction between nitric acid and either phenyl- or hydroxymethyl-o-carborane derivatives yields products where the nitration is directed toward the substituent and not the carborane cage. Thus, 1-hydroxymethyl- and 1,2-bis (hydroxymethyl)-o-carborane is converted to the highly explosive 1-nitrato- and 1,2-dinitrato-o-carboranes, respectively, by treatment with cold nitric acid [85]. Rather encouragingly, 1-phenyl-o-carborane reacts with 100% nitric acid or with a mixture of nitric and sulfuric acids in an inert solvent, forming predominantly 1-(p-nitrophenyl)-o-carborane [86]. Interestingly, nitroso derivatives o-carborane have been synthesized from lithium-o-carboranes and nitrosyl chloride at very low temperatures [87].

Poly(azophenylene-o-carborane) has been prepared from diphenyl-o-carborane by means of nitration, reduction, and acylation to initially give 1,2-bis-(N-nitroso-acetylaminophenyl)-o-carborane (NAFC). Rapid decomposition in solution affords phenylene amino phenyl carborane (PAFC) synthesis by recombination of phenylene and azophenylene radicals [88]. These radicals have also been utilized to form copolymers of carborane-containing copolymers from monomers polymerizable via radical mechanisms. Thus, copolymers of polystyrene and poly(azophenylene) can be read-

ily formed by means of emulsion copolymerization of styrene with NAFC decomposition products.

2.4. Polyphosphazene-Based Energetic Binders

Polyphosphazenes are new polymers with unique properties, which include a combination of high temperature stability, low temperature flexibility, low surface energy, biofriendliness, and inflammability. The energetic binders are typically linear carbon-chain polymers which display low energy densities and relatively high glass transition temperatures T_{gl}. The high T_{gl} of the binder requires the addition of a suitable plasticizer to the final PBX formulations in order to lower the T_{gl} to an acceptable level [89]. Although plasticization is a viable solution to ameliorate the binder's high T_{gl}, it also leads to the migration of the plasticizer [90] to the surface of the explosive filler, resulting in serious difficulties.

One of the main problems with energetic binders is therefore the difficulty in developing materials which display high energy-densities and low glass transition temperature, a combination of properties which would ultimately allow producing the formulation of PBXs of higher solids loading and yet good physical properties and low sensitivity.

In search of a viable alternative to carbon-based binders, novel systems based on a linear polyphosphazene backbone [91] are currently under investigation as potential high-density, high-energy-density (HED), and low T_{gl} binders for new, polymer bonded explosive formulations. Polyphosphazenes are polymer materials based on a formally "unsaturated" phosphorus-nitrogen backbone which can contain up to a maximum of 15 000 —R2P=N— units [92]. The final molecular weight of the polymer and its polydispersity [93] depend on the synthetic route adopted for its preparation. Like silicones and polysilanes, polyphosphazenes are semi-organic polymers having the repeat unit —R2P=N— (R can be a halogen, an organic group or an organometallic unit).

The synthesis of novel, high-energy phosphazene based binders for PBX formulation has been attempted by various workers over the last two decades. The first reported case focused on the synthesis of energetic cyclic compounds such as cyclotriphosphazene polynitramines [94], which can be prepared by the reaction of hexachlorocyclotriphosphazene (HCTP) with 1,2-diaminoethane and subsequent selective nitration of the amino groups of the product. Although generally obtained in good yields, these compounds were found to be highly heat and impact-sensitive, to the extent that even small samples had to be handled behind a protective shield

3. ENERGETIC PLASTICIZERS

Conventional plasticizers used with HTPB, namely, phthalates, dioctyl adipate (DOA), and isodecyl pelargonate (IDP) have also found applications with energetic binders. From the point of view of augmenting the energetics, a large number of compounds containing nitro, azido, nitrato group are emerging as potential plasticizer candidates.
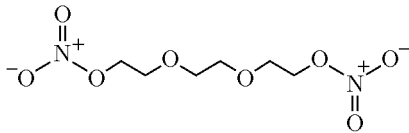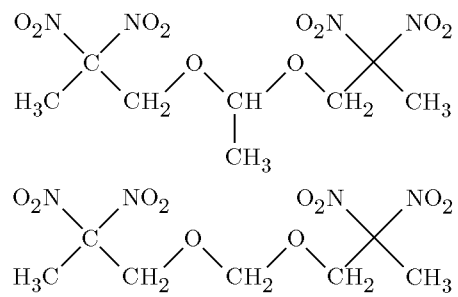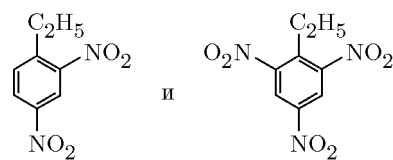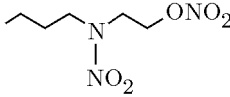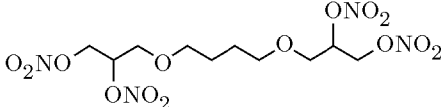
The primary role of energetic plasticizers in energetic material formulations is to modify the mechanical properties of the charge to improve safety characteristics. This is achieved by softening the polymer matrix and making it more flexible. In addition to improving properties of propellants such as tensile strength, elongation, toughness, and glass transition temperature T_{gl}, the plasticizer can have secondary roles. These roles include a reduction of mix viscosity to ease processing, modification of oxygen balance and energy content, and in the case of propellants, burn rate modification to tailor ballistics [95].

By their own nature, plasticizers are typically oligomeric materials that have number average molecular weights ranging within 200–2000. Plasticizers with molecular weights above 2000 tend to be viscous, with properties more akin to the polymer matrix. Plasticizers with molecular weights below 200 may be more effective in reducing T_{gl}, but they are highly volatile and tend to migrate out of a formulation readily (exudation). Plasticizers with number average molecular weights within 400–1000 are considered to give optimum plasticizing effect. Like their polymer counterparts, plasticizers can be inert (non-energetic) or energetic [96]. Non-energetic plasticizers are effective in improving mechanical properties, but degrade the energy output of the formulation by reduction of the overall oxygen balance. Examples of non-energetic plasticizers include esters, acetyl triethyl citrate, diethyl adipate, diethyl sebacate, and dioctyl adipate. Similar improvements in mechanical properties are desired from energetic plasticizers, but with a contribution to the oxygen balance and/or energy of the formulation.

Energetic plasticizers are typically nitro compounds or nitrate esters. Structural similarity with the energetic polymer should facilitate incorporation; however one of the most common problems has been exudation, i.e., migration of the volatile low molecular weight plasticizer to (and from) the surface of the formulation. Migration of plasticizers is a major obstacle to the use of energetic binders in explosive and solid propellant formulations. A promising recent approach has been to increase the structural similarity and, hence, miscibility by using oligomers of the polymer matrix as the plas-

Table 6. Energetic plasticizers [96]

Common name	Chemical name	Structural foprmula
NG	Nitroglycerin	CH_2ONO_2 $\vert$ $CHONO_2$ $\vert$ CH_2ONO_2
MTN	Metriol trinitrate	CH_2ONO_2 $\vert$ $H_3C-C-CH_2ONO_2$ $\vert$ CH_2ONO_2
TEGDN	Triethylene glycol dinitrate	(structural formula)
EGDN	Ethylene glycol dinitrate	CH_2ONO_2 $\vert$ CH_2ONO_2
BTTN	Butane-1,2,4-triol trinitrate	ONO_2 $\vert$ $O_2NOH_2C-CH-CH_2-CH_2-ONO_2$
BDNPA/BDNFA	Mixture of bis-(2,2-dinitropropyl)acetal and bis-(2,2- dinitropropyl)formal	(structural formula)
GAPA	Glycidyl azide polymer azide	$N_3-CH_2-CH_2{\Big[}O-CH_2-CH{\Big]}_{n\geqslant6}N_3$ with CH_2-N_3
K10	Mixture of 2,4-dinitro ethyl benzene and 2,4,6-trinitro ethyl benzene (65/35)	(structural formula) и (structural formula)
NENA	Alkyl nitrato ethyl nitramine	(structural formula)
GLYN (dimer)	Glycidyl nitrate (dimer)	(structural formula)

ticizer. It has recently been proposed to design plasticizers that closely resemble the polymer matrix, enhancing physical and chemical compatibility and, hopefully, minimizing the migration of the plasticizer. The structural formulas of energetic plasticizers are shown in Table 6.

3.1. Nitrate Ester Plasticizers

The first energetic plasticizer for commercial explosives was nitroglycerine (NG) or glycerol trinitrate, a high performance nitrate ester. First discovered in 1846, nitroglycerine is a sensitive explosive easily initiated by friction and impact. When heated above 200°C, it will explode, while upon storage it proves unstable at temperatures exceeding 70–80°C [97]. In addition, NG exhibits significant physiological effects, causing dilation of the arteries and severe headaches. Nevertheless, nitroglycerine still remains an effective plasticizer for many applications.

The nitrate esters have proved to be a fertile source of energetic plasticizers. Some of the major nitrate esters in use today include trimethylol ethane trinitrate (MTN or TMETN), triethyleneglycol dinitrate (TEGDN), ethyleneglycol dinitrate (EGDN or nitroglycol), and butanetriol trinitrate (BTTN). Being structurally similar to NG, they were developed to replace this material; most of these molecules possess some of NG. MTN or TMETN is chemically stable, insoluble in water and has low volatility. TEGDN is also chemically stable and has less impact sensitivity than NG and is less volatile than EGDN. EGDN is a more efficient plasticizer of nitrocellulose than NG, has more energy but is also sensitive to impact. It possesses a lower density and a greater volatility than NG. BTTN is often used in propellants as a replacement for NG. It has a lower density than NG but offers improved stability. Most of the energetic nitrate esters are HD 1.1 explosives that possess low critical diameters, high volatility and high sensitivity, making them difficult to handle.

3.2. BDNPA/F Plasticizers

Plasticizers composed of bis-(2,2-dinitropropyl)acetal (BDNPA) and bis-(2,2-dinitropropyl)formal (BDNPF) have found widespread application in energetic formulations. For example, US Army applications such as the M900 tank program, LOVA gun propellant, and the insensitive HMX-based explosive PAX-2A all use BDNPA/F as an energetic plasticizer.

BDNPA/F plasticizers are typically a 50/50 BDNPA/BDNPF mixture. Formal is a solid, slightly less energetic than liquid acetal and is used to form an eutectic to lower the melting point (making plasticizer useable at lower temperatures) [99]. BDNPA/F

Table 7. Physicochemical properties of GAP-diol and GAP-triol [82]

Characteristics	GAP-diol	GAP-triol
Density, g/cm^3	1.29	1.29
Heat of formation, J/g	1167	1167
Molecular weight	1700 ± 300	⩾900
Number of functional groups	2.0	2.5–3.0
Stability in vacuum, ml/g (200 h, 100°C)	⩾3	⩾3
Glass transition temparture, °C	−45	−45

was first developed by oxidative nitration of nitroethane to 2, 2-dinitropropanol (DNPOH) with silver nitrate as catalyst [100]. This nitration process was uneconomical because of problems with waste and loss of silver (≈1%), and it was modified further to include a selective chlorination step of nitroethane to 1-chloronitroethane. By replacing chlorinated solvents with methyl-tert-butyl ether (MTBE), the process has now been made environmentally friendly. The nitration is also now carried out with inexpensive persulfate salts as oxidant and potassium ferricyanide as catalytic additive. Furthermore, the synthesis of BDNPA/F is now automated and runs continuously to give high output of product [101].

BDNPA/F exhibits poor plasticizing properties in terms of lowering the glass transition temperature and viscosity of uncured PBX formulations. Furthermore, BDNPA/F may become unstable under severe conditions, such as a combination of elevated temperatures (>74°C) and high shock loading.

3.3. Azido Plasticizers

The poor mechanical properties of azide functional polymers like GAP can be improved markedly by incorporation of energetic azido functional plasticizers. The synthesis of low-molecular-weight azido polymers such as GAP plasticizers can be achieved in a single process involving azide displacement of chlorine from epichlorohydrin monomer (ECH) followed by polymerization without the need for a catalyst [102]. GAP plasticizers are compatible with GAP polymers and nitrate esters such as butanetriol trinitrate (BTTN) and trimethylol ethane trinitrate (TMETN). Properties of GAP diol and triol plasticizers are given in Table 7.

The plasticizing effect will be lost if the terminal hydroxyl groups on the plasticizer react with the isocyanate cross-linking agent, effectively tying the plasticizer into the cross-linked polymer matrix. Ample-

man [103] developed the synthesis of an azide terminated glycidyl azide plasticizer (GAPA), which has no reactive terminal hydroxyl groups available for isocyanate cure. GAPA is a pale yellow liquid with low molecular weight, low glass transition temparture, and good stability.

3.4. K10 Plasticizer

K10 plasticizer, also known as Rowanite, is a nitroaromatic plasticizer [104] consisting of a mixture of 2,4-dinitroethylbenzene and 2,4,6-trinitroethylbenzene (65/35). K-10 is manufactured by Royal Ordnance in the UK, and finds use as an energetic plasticizer in polymer bonded explosives. K-10 is a clear, yellow (or orange) liquid with an UK hazards classification of 6.1 (toxic). Compatibility issues with K-10 include sensitivity to lead azide and other primary explosives.

3.5. Nitratoethylnitramine Plasticizers

Nitratoethylnitramines (NENAs) are effective plasticizers in energetic formulations, particularly, in nitrocellulosic systems. NENAs contain both nitrate ester and nitramine functionalities. NENAs have been known since the 1940s, when DINA (dinitroxy ethyl nitramine) was scaled-up for use in Navy flashless gun propellants [97]. It was not until the late 1970s that researchers at Eglin AFB used NENAs in gun propellants that required low flame temperatures and low molecular weight [105]. NENAs are readily manufactured by nitration of commercially available alkyl ethanolamines in high yields (80%).

The use of NENAs as plasticizers in gun and rocket propellants provides excellent properties such as high burning rates, reductions in flame temperature and product gas molecular weight, and higher specific impulse (based on moderate loadings of 60–70% RDX in a nitrocellulose/NENA binder). NENAs plasticizers possess good thermal stability, readily plasticize nitrocellulose and other polymers, generate low-molecular-weight combustion gases, and give moderate impact sensitivity [106]. One disadvantage of NENA plasticizers is potential incompatibility with ammonium perchlorate [95]. In the past, the same problem for ammonium perchlorate and nitrate has been resolved by the inclusion of free radical scavengers (free radical traps), 2-nitrodiphenylamine or alkaline additives such as sodium bicarbonate. Neither has proved as effective for NENAs.

3.6. Oxetane Plasticizers

A recent approach has been to design plasticizers that closely resemble the polymer matrix to increase the physical and chemical compatibility and reduce the migration of the plasticizer. Linear NIMMO oligomers (polymers monomer units) were therefore prepared for use as plasticizers in polyNIMMO binder systems [95]. Oligomeric NIMMO has a lower glass transition temperature than the cyclic tetramer but still contains NIMMO monomer. In order to remove the terminal hydroxy groups and prevent unwanted reaction with the isocyanate cross-linking agent, oligomeric NIMMO has been further nitrated (nitration also increases the oxygen balance and enhances the energy of the binder system) [15]. Nitration with N_2O_5 for 30 min at 10°C gives clean conversion to nitrato terminated oligomers without sign of chain scission. Nitration with excess N_2O_5 also converts residual NIMMO monomer into TMETN.

3.7. GLYN Dimer Plasticizer

The linear GLYN dimer molecule is significantly smaller than polyGLYN [107]. As with the NIMMO oligomer, nitration increases oxygen balance and energy content and prevents unwanted reaction of the plasticizer with isocyanate. GLYN dimer is normally a mixture of oligomers and has a low glass transition temperature (−64.9°C) and impact sensitivity compared with nitrate esters such as BTTN and TMETN. GLYN dimer also has a calculated explosive performance superior to K10, BuNENA, and BDNPA/F. Initial studies of polyGLYN with GLYN dimer as plasticizer have produced well-cured binders with good mechanical properties. It is anticipated that the GLYN dimmer will be less susceptible to migration than conventional plasticizers.

CONCLUSIONS

The development of high-energy gas-generator systems remains a challenge. Ways of its solution are presented in reviews [108, 109], where it is shown that to achieve the maximum energy efficiency of solid propellants, it is necessary to optimize the parameters of each component of the mixture, as well as the mass content of the components. In doing so, one should take into account the multi-purpose functions of the binder, which should provide proper rheological parameters of the propellant mass, making it possible to employ the casting technology, and should provide the mechanical parameters of the cured propellant, allowing it to be used effectively at a variable initial temperature and operating overloads. At the same time, the binder should produce combustion products with minimum molecular weight and have a high enthalpy of formation. It should be noted that, according to theoretical estimates [110], the use of an active binder of the type $(C_xH_yN_zO_e)_n$ with

an enthalpy of formation $\Delta H_f = 42$ kcal/kg (175 J/g) in a solid propellant containing hypothetical oxidizer with $\Delta H_f > 800$ kcal/kg (3333 J/g) completely eliminates the need to include a metal fuel (aluminum) in the propellant. This propellant will have a high specific impulse, making it possible to solve the problems of two-phase losses of specific impulse and erosion wear of the nozzle throat. However, this problem has not yet been solved, and it takes considerable efforts of synthetic chemists and technologists to achieve positive results.

It is known that at the initial stage of development, simplest hydrocarbon binders, starting with bitumen, were used in composite rocket propellants. Subsequently, inert binders were replaced by active or energetic binders. Historically, the efforts of foreign researchers have been directed toward the development of unitary energetic binders (GAP, BAMO, etc.), while the work of Russian researchers has focused on the use of energetic plasticizers with high-enthalpy inert binders. Comprehensive information on achievements in the field of energy-saturated polymers is contained in recently published monographs [95, 111].

It should be noted that the requirements for the characteristics of energetic polymers in designing explosives with a polymer binder are less stringent than in the case of solid rocket propellants. This is due, in particular, to the fact that the polymer content in PBX is significantly lower than that in propellants, and it is not required to provide various physico-mechanical characteristics and an increased oxygen balance of the system. Accordingly, the replacement of an inert polymer by an active polymer often does not improve the performance of PBX. However, the use of active polymers can be effective for increasing the strength of an explosive charge without loss in its energy content.

The modern PBX production technology should be developed and improved in compliance with environmental safety requirements. In particular, this concerns the use of toxic organic solvents. A new way to produce PBX without organic solvents was recently proposed in [112]. The absence of environmentally harmful solvents (for example, dichloromethane, CH_2Cl_2) in the working cycle reduces the environmental damage from the production of explosives. The working process is based on the use of the thermosensitive material poly-N-isopropylacrylamide (polyPNIPAM), which dissolves well in water at a temperature below the critical temperature ($\approx 32°C$) and exhibits hydrophobic properties at higher temperature. Individual polymer chains begin to form colloidal aggregates with the inclusion of explosive particles. The resulting plastic explosive has a reduced impact sensitivity. In particular, for a PBX

consisting of 97.5% CL-20 and 2.5% PNIPAM, the drop-weight impact height for detonation initiation is twice that for (97.5/2.5) CL-20/Estane PBX manufactured by classical technology with the evaporation of organic solvents.

Another method of environmentally safe production of low-sensitivity PBX is described in [113]. Chlorinated paraffin is proposed as a binder, making it possible to eliminate the use of plasticizers, which impair the integrity and performance of PBX. Chlorinated paraffin has several advantages over typical binders. It is a viscous liquid with a high boiling point (or the boiling point is absent) and a low glass transition temperature ($-50°C$) and has the properties of a Newtonian liquid, maintaining a constant viscosity during compaction. Chlorinated paraffin has high adhesion to explosive crystals and fire-suppressing properties. The impact sensitivity of PBX containing 6% chlorinated paraffin (52% Cl) was found to be low: in a test with an aqueous layer, detonation was initiated at a pressure of 26 kbar.

Another innovation in the production of PBX is the use of click chemistry. Click reactions for the synthesis of new energetic plasticizers are described in [27]. It is planned that such plasticizers will be used in the production of cast PBX and will increase the energy content of PBX. It has been found that the new reactive plasticizers work like traditional plasticizers at the initial stage of preparation of the fuel mixture, but then, by means of a click reaction, they are involved in the cure of the polyurethane binder. This reaction acts on the alkyne groups of the plasticizer and on the azide groups in the prepolymer, for example, glycidyl azido polymer. The ability of the plasticizer to react with the prepolymer matrix leads to the absence of exudation of the plasticizer even at its relatively high content in the binder. At the same time, its explosophoric groups C—NO_2 and N—NO_3 are more stable than the —N_3 and O—NO_2 groups.

There has been extensive research in the field of high-energy polymers, including theoretical studies of physicochemical transformations at various levels of detail. Thus, the mechanical properties of ε-CL-20, HMX, and TATB based PBX containing various fluoroplomers as binders have been studied [115] at the micro-level using molecular dynamics methods. It has been found that the mechanical properties depend on the type of crystalline plane of the explosive which is in contact with the binder. In particular, for ε-CL-20, the magnitude of the adhesion force varies in the series (001) $>$ (100) $>$ (010). This implies that during wetting of CL-20, the fluoropolymer concentrates near the (001) face.

The thermal decomposition of RDX in the presence or absence of Estane polymer chains has been studied at the micro-level approach using the Reax FF method [116]. It has been shown theoretically that in the thermal decomposition of RDX, the presence of polymer chains reduces the rate of decomposition (the number of fragments) of the explosive molecule. The pressure of explosion of the RDX–polymer system turned out to be lower than that of pure RDX, due to the smaller number of fragments formed. The results of this simulation indicate a reduced sensitivity of the RDX–polymer system to thermal load.

Of great interest are the results of modeling the behavior of energetic systems at the mesolevel, whose scale is determined by the dimensions of heterogeneous components [117]. Although the release of energy during reaction of an energetic substance occurs at the molecular level, energy conversion to other forms (thermal and mechanical) occurs via a mesoscopic structure, resulting in so-called mesoscopic effects. Molecular dynamic simulation has made it possible to explain the mechanism of irreversible increase in the size of TATB crystals during cyclic heating of PBX. It has been shown [118] that the irreversible increase in the crystal size is not observed for individual TABT crystals, but occurs when crystals interact with each other in the presence of a binder. The simulation has also shown that the extent of the effect depends on the nature of the binder and can be significantly reduced by using CYTOP amorphous fluoroplymer. Interesting results have been obtained in modeling the isentropic loading of a mixture of binder and HMX crystals [119]. It has been found that initial deformation occurs mainly at the contact points of large grains of HMX and subsequent deformation takes place in the intergrain space in the volume of the binder. Initiation of the energetic system occurs in the zones of energy concentration (hotspots) formed as a result of plastic deformation of large HMX crystals.

Finally, modeling at the macroscopic level aims at predicting the mechanical behavior of PBX systems, which is complicated by the interplay between the mechanical characteristics of the polymer binder and the crystalline explosive. The fracture of PBX is primarily due to the rupture of the bond between the polymer and the explosive crystal. A continuous model of damage is not able to describe the interfacial fracture of PBX, and it is necessary to use a discrete model based on cohesive laws and suitable for studying interfacial fracture [120]. In the case of PBX, fracture on the polymer–crystal contact surface depends on the rate of loading due to the viscoelastic nature of the polymer binder. Along with the interfacial gap, fractionation of explosive crystals plays an important role in the fracture process. Furthermore, the crystals show different responses to deformation of different signs. For example, in tension HNX crystals behave like an elastic solid, whereas in compression, they show elastic-plastic behavior, which is described within a continual approach. Thus, the mechanical behavior of the PBX should be modeled using a combination of the continual and discrete approaches [121].

It should be noted that the functioning of energetic materials is determined by the complex interplay of physicochemical processes, with widely differing spatial and temporal scales. The development of multiscale modeling methodologies for such processes is at an early stage [95, 122], and the task is to obtain correlations between the parameters of the atomic/molecular structure of the substance and its mesoscopic characteristics, and then macroscopic properties. For a deeper understanding of the behavior of energy-saturated polymers in solid propellants and explosives with a polymer binder, further theoretical and experimental studies of new energetic compounds are required, including the synthesis of selected compounds and evaluation of the ballistic characteristics of compositions on their basis.

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