Evaluation of GIM as a Greener Insensitive Melt-Cast Explosive

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ABSTRACT

For years, DRDC Valcartier has invested efforts at developing energetic thermoplastic elastomers (ETPEs) based on linear glycidyl azide polymers (GAPs) to serve as energetic binders, and replace thermoset matrix in insensitive explosives. It was first observed that introducing ETPEs in their melted form was not an easy task because high and non-practical viscosities were encountered in the process. It was discovered that TNT could be used in its melted form as an organic solvent to dissolve the ETPE and allow its incorporation into the insensitive formulations. Using these ETPEs led to the development of a greener insensitive melt-cast explosive named GIM. This new explosive was intensely studied. The mechanical properties and proportions of ETPE in the formulations were optimized to obtain a melt-cast with low viscosity while leading to an insensitive explosive formulation. Work was conducted on GIM explosive to test its performance and sensitivity, its fate and behaviour into the environment, its recycling capability, and its toxicity. This paper describes the results of all experiments conducted so far to test these aspects of the GIM explosive. The preparation of the ETPEs and the GIM explosives will also be briefly described.

Keywords: thermoplastic, elastomer, GAP, XRT, GIM

NOMENCLATURE

BAMO: Bis 3-azidomethyl oxetane
BRI-NRC: Biotechnology Research Institute - National Research Council
C4: Demolition explosive made of 91% RDX and plasticizer in polyisobutylene
CL-20: 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane
DADNE: 1,1-diamino-2,2-dinitroethene
DNAN: Dinitroanisole
DOA: Dioctyl Adipate
DRDC: Defence Research & Development Canada

EC$_{20}$: Effect concentration which causes a 20% inhibition
EC$_{50}$: Effect concentration which causes a 50% inhibition
ETPE: Energetic thermoplastic elastomer
FOX 7: Same as DADNE
FOX 12: N-guanylurea-dinitramide
GAP: Glycidyl azide polymer
GIM: Green Insensitive Munitions
HMX: High Melting Explosive, 1,3,5,7-tetranitro-1,3,5,7-tetrazine
HTPB : Hydroxyl Terminated Polybutadiene
INRS-ETE: Institut national de la recherche scientifique - Centre eau terre et environnement
IM: Insensitive Munitions
LC$_{50}$: Lethal concentration which causes a 50% mortality
NTO: 3-nitro-1,2,4-triazol-5-one
PBX: Plastic bonded explosive or polymer bonded explosive
RIGHTTRAC: Revolutionary Insensitive, Green and Healthier Training Technology with Reduced Adverse Contamination
RDX: Research & Development Explosive, 1,3,5-trinitro-1,3,5-triazine
SERDP: Strategic Environmental R&D Programme
TDP: Technology Demonstration Program
TNT: 2,4,6-Trinitrotoluene
XRT: eXperimental Rubbery TNT

INTRODUCTION

For the last two decades, insensitive explosives development has been at the heart of R&D work in most military organizations. More recently, the development of insensitive explosives raised in importance in Canada because these explosives are safer for the Canadian Forces personnel and they allow interoperability between the allied Forces. In many countries, efforts are being made to develop and field new insensitive energetic formulations. As an example, the USA has recently developed and put into service an insensitive explosive based on 2,4-dinitroanisole (DNAN) and 3-nitro-1,2,4-triazol-5-one (NTO) but little is known about the environmental toxicity, fate and behaviour of these compounds (Di Stasio (2009), Niles and Doll (2001), Fung *et al*. (2009) and Samuels (2009)). Because of that, many other explosives are evaluated as potential TNT and RDX replacements. Furthermore, because of the environmental impacts of munitions and energetic materials in general, formulations now need to be greener, meaning that their environmental footprint should be lower than existing formulations. There is still a lot of work to be conducted before the best green and insensitive melt-cast explosive formulation is identified and accepted by the formulators, the managers, and the people concerned by environmental impacts.

The development of insensitive explosives can be separated into two main technologies based on the processes to produce them. The first process involves the use of a cast-cured polymer-bonded system. These explosives are called "cast-cured explosives" or often "plastic or polymer bonded explosives" (PBX). This type of explosives used to dominate the IM explosive development. The second type of explosives is the melt-cast explosive. In this case, the explosives are melted and cast into shells. More recently, there has been an increased interest for insensitive melt-cast explosives, mostly based on DNAN and NTO. This renewed interest for insensitive melt-cast

explosives is related to their lower costs and ease of production, as presently, most of the manufactured explosives are made by melt-cast technology. Furthermore, melt-cast technology is mature and well understood, and as a result, there are much more industrial melt-cast facilities than any other types of casting. While PBXs were previously used in large high-cost items, such as missiles or bombs, new uses have been identified in smaller weapons such as mortars or artillery shells. Pelletier *et al*. (2009) presented a good example of this in the demonstration of the French RDX/HTPB-based HBU88B in the U.S. 120 mm mortar. New PBX formulations are also being created with tailored properties for specific applications, such as boosters or for blast. They either make use of older explosive crystals known for their insensitive properties, such as NTO or use new promising molecules such as 1,1-diamino-2,2-dinitroethene (DADNE, FOX-7), N-guanylurea-dinitramide (FOX-12) or 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) (Anderson *et al*. (2009), Bergman *et al*. (2009), Hatch *et al*. (2009), Nouguez and Mahé (2009) and Spyckerelle and Eck (2009)). Compared to melt-cast explosives, the cast-cured PBXs are more difficult to process, to recycle, and are generally more expensive.

In 1988, DRDC Valcartier started investing efforts in the development of insensitive energetic materials. At this time, environmental pressure and the need for interoperability between allied armies gave the momentum for this new area of research. It was soon realized that formulating energetic materials that would be insensitive, environmentally friendly and produced at low costs was not an easy task. Many efforts were done worldwide to work with glycidyl azide polymer (GAP) as an energetic binder. In 1995, radioactive carbon-14 GAP was prepared to evaluate its degradability (Ampleman *et al*. 1995). It was demonstrated that GAP although insoluble in water was mineralized at 10-20% by indigenous microbes (Jones *et al*. 1996). Later in 2004, ATK Alliant techsystems conducted a study for SERDP where they found that ETPEs based on GAP and poly BAMO were non toxic to mice (Cohen et al. 1004). Ampleman *et al*. (2002) developed at DRDC Valcartier new energetic thermoplastic elastomers (ETPEs) based mainly on linear GAP to give the insensitive character to the formulations. These energetic thermoplastic elastomers were prepared by using GAP as macromonomers reacted with 4,4′-methylenebis(phenyl isocyanate). By doing so, energetic copolyurethane thermoplastic elastomers were obtained, and these rubbery physically cross-linked matrixes were mixed with secondary explosives which provided the basis for a new generation of insensitive explosives. Many approaches were taken to develop ETPEs and the complete description of GAP, their synthesis, and the ETPEs obtained from them were published (Ampleman *et al*. (1988, 2010)). Later, the toxicity of these ETPEs was evaluated and it was demonstrated that they were non toxic and could be considered as a green ingredient (Monteil-Rivera *et al*. 2008).

The original objective of the ETPE project at DRDC Valcartier was to develop ETPEs that could melt at 85ºC, and behave as a GAP-cured system to replace 2,4,6-trinitrotoluene (TNT) in melt-cast formulations. The main problem of incorporating these ETPEs into melt-cast insensitive explosive formulations resides in the fact that the melt-cast process is a solvent less process and, in such cases, once melted, ETPEs would give very high mix viscosities. Furthermore, our copolyurethane thermoplastic elastomer decomposes before melting. It was found that melted TNT could act as an organic solvent and was able to dissolve the ETPE matrix resulting in acceptable processing viscosities. A new insensitive explosive was then prepared. It is only later that the green character became very important because nowadays, it would be unwise to develop an explosive that has a negative environmental footprint.

It is known that TNT is toxic and the environmental fate and transport of TNT were demonstrated by Sheramata *et al*. (1999) and Monteil-Rivera *et al*. (2009). They showed that in the environment, this explosive degrades rapidly by photolysis or biotransformation into 2-, and 4-aminodinitrotoluene and other metabolites that form covalent bonds with organic matter of soils, making it not bioavailable. This means that TNT, once released in the environment, reacts and cannot reach ecological or human receptors, making it less environmentally threatening when used in live firing activities. This was demonstrated on anti-tank ranges in Canada by Mailloux *et al*. (2008), as high concentrations of HMX were observed while no TNT was, even if the explosive formulation used there was Octol, which is based on both compounds. The idea of dissolving the ETPE in melted TNT was therefore studied and resulted in the development of an insensitive explosive named "XRT" for "eXperimental Rubbery TNT". This explosive was obtained by mixing the ETPE with Composition B. However, the nitramine RDX has proven to be both toxic and highly mobile in the environment, while HMX is much less soluble, toxic and mobile. Replacing RDX by HMX using Octol instead of Composition B led directly to the development of a new greener insensitive recyclable explosive (GIM). For this explosive, Ampleman *et al*. (2003) used GAP of molecular weight 2000 as macromonomers to obtain the best mechanical properties and melted viscosity for the copolyurethane thermoplastic elastomers used for the GIM preparation. Diaz *et al*. (2001) studied the structure of the ETPE and confirmed that the best candidate was obtained with GAP 2000. Because ETPEs are recyclable, an easier disposal and reuse of the formulations at the end of their life cycle can be accomplished.

More recently, a Technology Demonstration Program (TDP) named RIGHTTRAC, which stands for "Revolutionary Insensitive Green and Healthier Training Technology with Reduced Adverse Contamination", was initiated using greener explosives (such as GIM), greener propellants and a self-destructive device system to produce a greener weapon. A tremendous amount of work has been dedicated to these compounds, in particular to the GIM explosive. This paper describes the preparation of the ETPEs, the XRT and mostly the greener explosives GIM. The paper will also present results of the performance characterization, the IM character, the fate and environmental behaviour that encompass dissolution rate, transport and fate in soil and in water, and toxicity measurements.

SYNTHESIS, IM TESTS AND VARIOUS OTHER TESTS

Synthesis of ETPEs

The preparation of ETPE 2000 was described earlier by Ampleman *et al*. (2002 and 2003) and Diaz *et al*. (2001). The most important factor to consider in these syntheses is the dryness of the reactants and reaction mixture. Water should be avoided in the reaction and a precise NCO/OH ratio must be observed to get the desired and highest molecular weight for the linear copolyurethane thermoplastic elastomer. When water is present, carbamic acid is formed and upon decarboxylation, an amine is formed reacting 100 times faster with isocyanate than the secondary hydroxyl groups of the macromonomer. As a result, chemical cross-linking is formed and lower molecular weights are observed, which renders the polymer insoluble. Having a NCO/OH ratio greater than one would also result in chemical cross-linking from allophanate and biuret bond formation while a NCO/OH ratio lower than one would result in lower molecular weight and may give unwanted behaviour as it will be described later. Years ago, 3M was interested in producing our ETPEs based on GAP prepolymers and is at this moment the only source for these products. For the RIGHTTRAC program, a commercial sample prepared by 3M

in Minnesota was used for the preparation of the GIM explosives. This sample was prepared using a GAP macromonomer having a molecular weight (M_w) of 2400 g/mol.

Synthesis of XRT and GIM explosives

The first formulations of XRT explosives were carried out using a concentration of ETPE 2000 of 10% (Ampleman *et al*. 2003). After refinement of the process and adjustment of the viscosity of the melt-cast mixes, the best results were obtained with a concentration of ETPE 2000 of 6%. The ETPE 2000 was dissolved in melted Composition B and the mixture was stirred until homogeneity was obtained. The resulting mixture could be poured on a flat surface to make what we refer to as "cookies" upon cooling that could be used later in the filling of shells or, could be poured directly into shells.

The development of the XRT explosives led directly to the preparation of greener insensitive munitions (GIM) explosives using melted Octol instead of Composition B. HMX is considered more environmentally friendly due to its lower solubility and toxicity. Moreover, as already mentioned the ETPE is also considered green. In the case of the GIM explosive, the preparation and procedures were almost identical but this time, the concentration of the ETPE 2000 was adjusted at 9.5% to obtain the best results. The concentration of ETPE is a key parameter and must be adjusted to obtain the best IM properties while keeping the melt-cast viscosity at the lowest level possible to allow the use of industrial melt-cast facilities while minimizing the HMX sedimentation. Most efforts were done on the GIM explosive. The following results are related to GIM rather than XRT even if they are very similar.

In the RIGHTTRAC TDP, two candidates were evaluated for the green explosive, a PBX and the GIM explosive. The GIM explosive was chosen based on its energy, performance, IM characteristics and environmental footprint. The plastic-bonded explosive (PBX) used for comparison is a Canadian composition called CX-85. The explosive is made of 84.25% HMX and has an HTPB/DOA binder system cured with isophorone diisocyanate (IPDI). The surface agent system is proprietary. The whole formulation is a small modification of compositions presented before by Hooton (1992). This explosive was deemed a good generic PBX with a decent performance compared to Composition B (because of the HMX) and hence was tested at the same time as the GIM for comparison purposes.

IM tests on explosives

IM tests were conducted at DRDC Valcartier mainly with 105 mm shells filled by either GIM or PBX (CX-85). These tests were also conducted on 105 mm filled with Composition B for comparison. Bullet impact, sympathetic detonation, shaped charge jet and slow cook-off tests were made and the results were analysed based on a scaling from 1 to 5 and overpressure collected according to Annex A of various NATO STANAGs (2003 a, b and c) and (2004).

Bullet impact

The weapon used for these tests was 0.5 in. armour piercing and the bullet velocity was 850 ± 30 m s^{-1} as described in STANAG 4241 (2003 a). Evaluation of the reactions was done using the air overpressure and characterisation of the fragments collected (STANAG 4241 (2003 a)). Composition B presented type 1 and 2 reactions and failed the test while GIM and PBX led to

type 5 reactions and passed the test. Figure 1 shows that the bullet passed through the shell without reaction in the GIM shell.

Figure 1: Bullet impact result on GIM explosive.

Sympathetic detonation

During the test, a shell was used as a donor and another was used as an acceptor. Two other witness empty shells were placed in the assembly for confinement (Figure 2). To evaluate the result, an overpressure sensor was used to measure air pressure. Outcome evaluation was also made by characterizing the size of the fragments collected, in accordance with Annex A of STANAG 4396 (2003 b). The projectile with the white cap (C4) is the donor and the acceptor is the one with fluorescent orange color. The other projectiles were empty and were used only for confinement. Composition B and GIM had type 3 reactions and passed the test while PBX had no reaction and also passed the test.

Figure 2: Sympathetic detonation set-up.

Shaped charge jet

The test was conducted with the set-up illustrated in Figure 3. The shaped charge was fired and the jet was oriented and directed to the shell. The air pressure measurement was performed by overpressure sensors. The result evaluation was carried out by these pressures and the size of fragments collected. In all cases, type 1 reaction and multiple fragments were obtained and none of the formulations passed the STANAG 4526 test (2004).

Figure 3: Shaped charge test set-up.

Slow cook-off

The test was conducted using an oven in which the temperature was measured at the bottom and front, top and rear, top and center and also in the explosive inside the shell (Figure 4).

Figure 4: Oven set-up for the slow cook-off.

The heating of the sample was done as follows: the experiment started at room temperature and the temperature was increased to 100°C in 30 min, then, maintained for 90 additional min. A heating rate of 25°C h^{-1} was then applied until a reaction occurred. Pressure sensors were installed to measure the overpressure, but no values were observed since only burning reactions were obtained. The evaluation of the results was done visually according to STANAG 4382 (2003 c).

Unexpected results were observed for the PBX formulation. In this case, the explosive slowly extruded out of the shell pushed out by an important quantity of gas formed during the heating period. The extruded material appeared cracked and porous. The released gases were flammable and ignited a fire upon contact with the heater. Following the gaseous ignition, the PBX started burning two and a half minutes later. The burning reaction appeared to start into the gas phase instead of the explosives which is not desirable. Nevertheless, type 5 reactions were observed for all formulations, including Composition B, and all formulations passed the test.

All the IM tests revealed that GIM and PBX have insensitive behaviour. In sympathetic detonation, the PBX behaved in a better way showing no reaction, but the GIM explosive passed the test with a type 3 reaction which is acceptable. For the slow cook-off, even if the PBX passed the test, the formation of flammable gases during the reaction is undesirable.

If these two explosives are insensitive, one would wonder if it is possible to blow them up using the conventional C4 blocks method. Recent experiments were conducted to blow-in-place 105 mm shells filled with GIM and PBX CX-85 in different set-ups. All the projectiles went high order using one C4 block (500 g) during the blow-in-place operations. These results will be published later. These experiments demonstrated that it is possible to have an insensitive explosive having a good performance, not reacting to unwanted stimuli and still responding to conventional destruction methods using a C4 block.

Stability and performance evaluation

In addition to the IM tests, XRT and GIM formulations were evaluated by vacuum stability tests, impact and friction sensitivity (BAM), density and viscosities of the melted mixes measurements. The viscosities were measured directly in the mixer equipped with a temperature control bath at 95° C using a Brookfield rheometer (model LVDV-III+). Helipath T spindles at sizes C and D were in with shear mode (Y) at 5,10, 15 and 20 RPM. Furthermore, performance and shock sensitivity tests (gap tests) were also conducted. All the results from these tests are found in Table 1.

Vacuum stability tests showed a maximum gas evolution for XRT and GIM of 0.8 mL cm^{-3}. Impact sensitivity tests gave for both XRT and GIM a 20 N m value compared to 10, 7.5 and 5 N m for TNT, Octol and Composition B respectively. The friction sensitivity tests gave 360 N for XRT and GIM compared to 80, 120 and 240 N for TNT, Octol and Composition B, respectively. Our best products obtained with Composition B mixed with ETPE 2000 at 6% w/w (XRT) and Octol mixed with ETPE 2000 at 9.5% w/w (GIM) have densities of 1.65 and 1.67 g cm^{-3}, and viscosities of 40 and 50 poises respectively.

Brousseau *et al*. (2004 and 2010) evaluated the performance and showed that the detonation velocity is 7689 m s^{-1} and 7726 m s^{-1} for XRT 6% and GIM, respectively. The detonation pressure was calculated at 24.2 GPa for XRT (92% of Composition B) and at 24.9 GPa for GIM (94% of Composition B). The plate dent test confirmed 91.2% Composition B for XRT and 96% Composition B for GIM with 0.76 ± 0.01 cm. Large scale gap tests revealed a value of 167 cards for XRT 6% while 188 cards were obtained for GIM. As a reference, Composition B has 217 cards for this test. The detonation velocity of the studied mixes is between 94% and 99% of that of Composition B, while the detonation pressure is between 81% and 96% of that of Composition B. In general, the results showed that the XRT and GIM formulations are stable, have a reduced sensitivity to impact and friction, reduced shock sensitivity compared to current melt-cast explosives, that their performance is good and their behaviour in rifle bullet tests is excellent (Diaz *et al*., 2001).

Accelerated aging

Recently, thermal testing was performed on the latest XRT and GIM melt-cast formulations. At the end of the one-week aging process at 70ºC, unacceptable exudation rate of the

copolyurethane was observed. After examining in detail the products in these formulations, it was concluded that the commercially produced ETPEs used in these formulations was not fully reacted and that higher molecular weights for the copolymers were needed to pass the exudation test. For the commercial producer, it was safer to do the polymerization reaction at a slightly lower NCO/OH ratio than one to ensure that no chemical cross-linking occurred in their batch reactor, but this resulted in a lower molecular weight of the copolymers and also a lower hard segment percentage. This resulted in a softer rubber that had less hydrogen bonds, which allows the exudation of the material. The synthesis of the ETPEs was repeated at DRDC Valcartier using GAP 2000 with an exact NCO/OH ratio equal to one, which led to a higher molecular weight copolymer and a higher hard segment content. No sensitivity testing was repeated since it is believed that higher molecular weights of the binder having the same structure would not give any differences in the sensitivity tests. As a result, the aging tests were repeated and practically no exudation was observed. Further work is going on to permanently solve this issue.

Recycling

An important aspect of using thermoplastic elastomers in insensitive explosive formulations is that they allow easy recycling compared to cast-cured PBXs (Poulin *et al.*, 2010, 2011 a, b). The most costly ingredients in the XRT and GIM are RDX or HMX. Upon heating, both XRT and GIM formulations can be melted and poured out of the shells if reclamation should be conducted. It was demonstrated that the XRT or GIM products can then be dissolved in ethyl acetate, resulting in the precipitation of the insoluble nitramines. The ETPE and TNT dissolve easily into ethyl acetate while the nitramines are insoluble. Upon filtration, the nitramines were easily recovered (99.9%). The analysis and spectroscopy of these recycled nitramines were identical to the original ingredients, therefore recuperation and reuse could be easily done. The filtrate contained the ETPE and TNT which could be separated using a Soxhlet with hot methanol as the extraction solvent (Diaz *et al.*, 2001).

ENVIRONMENTAL EVALUATION OF GIM

The release of munitions constituents and their transformation products from unburned deposited residues may lead to contaminated soils, surface water bodies or groundwater. These residues may be deposited upon firing or released from UXOs that were cracked, corroded or suffered low order detonations. Factors that govern the transport, fate and impact of these contaminants in soil include dissolution, sorption, abiotic transformation, biotransformation, volatilization, bioaccumulation, and toxicity. Our main collaborators from BRI investigated the behaviour of the complete GIM formulation and compared it to that of Octol (Hawari, 2009). GIM (HMX/TNT/ETPE: 51.5/40.7/7.8) was prepared at DRDC Valcartier and supplied to BRI for this study.

Dissolution tests

To evaluate dissolution and fate of TNT and HMX in GIM samples, batch and dripping tests were performed with GIM samples (Hawari, (2009), Monteil-Rivera *et al.*, (2010)). In batch experiments, the concentrations of TNT and HMX measured at equilibrium agreed well with the solubility values calculated for each component using the correlations previously established to relate aqueous solubilities of HMX and TNT with temperatures (Lynch *et al.*, 2001). Moreover, TNT dissolution rate clearly decreased upon renewing of the aqueous supernatant with fresh

distilled water, whereas the dissolution rate of HMX remained more or less constant throughout the successive washings. A similar phenomenon was previously observed by Lever *et al*. (2005) who reported that the slow dissolution of RDX controlled the dissolution of Composition B (RDX/TNT/wax, 60/39/1) particles by limiting the exposed area of TNT. In the present case, HMX, which is the major component of GIM, dissolved less rapidly than TNT and had its dissolution limited by its low solubility in water. As a result, the nitramine was left at the periphery of GIM pieces as the only explosive to dissolve while TNT got concentrated at the center of the pieces. The dissolution rate of TNT was hampered by its limited exposure to water. The total amount of TNT released during four sequential runs conducted at 29.3°C represented 98.4 % of the TNT initially introduced, thus suggesting that the presence of ETPE did not prevent TNT from dissolving from a GIM particle that was fully immersed in an aqueous solution. This phenomenon would take place in the case where GIM particles would fall into a small pond or other surface water bodies. The total amount of HMX released under the same conditions corresponded to 2.8 % of the HMX initially present. Attempts to detect any ETPE degradation products in the aqueous filtrate obtained at 22.5°C using LC-MS did not show any significant peaks when scanning from 200 to 3000 Da and using both positive and negative ionization modes, thus suggesting the absence of ETPE dissolution in aqueous solutions. This confirmed the green character attributed to these ETPEs.

In order to evaluate the long term changes in the composition of GIM and to understand the dissolution process, an experiment was set up where a parallelepipedic piece of GIM (115 mg) was deposited on a glass funnel and exposed to a continuous water flow maintained with a peristaltic pump at a rate of 0.5 mL min^{-1} corresponding to ~ 19 drops per min. Outflow samples were collected in glass flasks covered with aluminum foil and flasks were changed every 24 h for 3 weeks and then every 7 days for 49 weeks. Each water fraction was analyzed for TNT and HMX by HPLC-UV. For comparison, a similar experiment was conducted with an Octol particle but using a nylon mesh to hold the whole fragile solid in the funnel and applying the same water flow (0.5 mL min^{-1}).

The leakage of TNT and HMX from Octol or GIM particles was modelled using an equation based on Fick's diffusion law and on the retardation of the faster dissolving compound by the slower dissolving one, as initially proposed by Lynch *et al*. (2003). The model allowed predicting well the dissolution data of Octol but was less appropriate to fit the data of GIM, likely due to a physical transformation and rearrangement of the remaining solid. Indeed, it was found that upon TNT dissolution, the ETPE shrinks and tends to protect the constituents from further dissolution (Figure 5). A complete description and discussion of these results can be found in the literature (Hawari *et al* 2009, Monteil-Rivera *et al*. 2010).

These experiments demonstrated that GIM solubilized more regularly and more slowly than Octol. The presence of the energetic binder ETPE in GIM prevented particles from collapsing and retarded the dissolution of TNT and HMX by limiting their exposure to water. In GIM like in Octol, the dissolution rate of solid particles was governed by the compound that dissolved at a slower pace, *i.e.* HMX in Octol and HMX and ETPE in GIM. Despite the non-fully satisfactory predictions obtained for GIM, the present findings demonstrate that ETPE decreases the risks of explosives leakage from solid explosive particles. It should thus help maintaining non-exploded

particles intact in the field and hence facilitate their physical removal by environmental site managers.

Figure 5: Microscopic photographs of a piece of GIM before (left) and after 47 weeks (right) in dripping test

Transport of GIM and its components in two soils

Transport of GIM and its individual components was studied in batch and column experiments. Two soils were used: a sandy soil, named "DRDC-08" coming from DRDC training range that contains little organic matter and a Webster clay loam, named "WCL", provided by Edgewood Chemical Biological Center (ECBC). Both soils were described in Monteil-Rivera *et al*. (2011), together with typical batch and column experiments.

The octanol-water partition coefficients (K_{ow}'s) and the soil/water distribution coefficients (K_d's) were measured for HMX and TNT with DRDC-08 and WCL soils. Aerobic conditions were selected due to the aerobic nature of the DRDC-08 soil. The K_{ow} value of HMX was found to be approximately 30 times lower than that of the reported value for TNT, indicative of the larger affinity of the nitroaromatic chemical for organic matter (Johnson *et al*., 2009). Sorption experiments conducted with HMX or TNT and DRDC-08 soil yielded low K_d values (0.07 for HMX; 0.19 for TNT), suggesting a limited sorption of both chemicals onto this soil (less than 4% for TNT). TNT K_d was about one order of magnitude lower than other values previously reported by Monteil-Rivera *et al*. (2009) for TNT sorption in various soils, consistent with the low content of clay or organic matter in DRDC-08 soil. In contrast, HMX and TNT exhibited a stronger affinity for WCL soil. Despite a K_{ow} value for HMX more than 10 times smaller than that of TNT, K_d values of the same order (5.78 for HMX; 4.58 for TNT) were obtained for both chemicals with WCL soil. The higher content of clay in WCL soil (28% vs. 2% in DRDC-08 soil) along with the type of clay phases present in this soil are probably responsible for the stronger sorption of HMX. This result confirms our previous observation that clay rather than organic matter governs the immobilization of nitroamines such as RDX, HMX and CL-20 onto soil whereas TNT can bind in a lesser extent to both types of solid materials (Monteil-Rivera *et al*., 2003).

Column experiments were conducted using solutions of either HMX or TNT in both soils. Flow from top to bottom was selected to allow easy introduction and removal of the solid compositions. Sodium chloride was added as a tracer at a concentration of 5 mg L^{-1}. Soil column was saturated with a $Ca(NO_3)_2$ solution, and pore volume determined as the volume necessary to fill the packed column was found to be around 18 mL for each prepared column. The pure background electrolyte solution was replaced by solutions containing HMX (3.5 mg L^{-1}) or TNT (50 mg L^{-1}) and the tracer. For the column involving solid formulation, the regular flow was stopped, formulation powder (50 mg) was introduced on the top of soil between two layers of glass wool and Nylon membrane (125 μm), and flow was restored using a solution containing the tracer.

Breakthrough curves plotted on a time basis for HMX and TNT in DRDC-08 soil confirmed the high mobility of the two explosive components in the sandy soil. When a column experiment

was conducted with solid GIM deposited at the top, TNT and HMX also co-eluted with chloride ions, thus confirming their negligible retention on DRDC-08 soil. However, the concentration of each of the two energetic chemicals did not remain constant in the outflow samples. TNT concentration decreased fast throughout the experiment while HMX concentration decreased very slowly. These findings are in line with the dissolution processes observed in the dripping experiment thus suggesting that transport of TNT and HMX released from GIM particles in DRDC-08 soil is governed by dissolution. Mass balance calculation from outflow concentrations during the 56 h experiment yielded 11.7 % and 1.5 % releases of TNT and HMX, respectively, after 56 h from the total amounts present in the powder. The breakthrough curve for HMX in WCL soil showed a neat retardation in this soil compared to the chloride ion, in agreement with the higher K_d value measured in WCL soil.

In conclusion, neither TNT nor HMX was retained by DRDC-08 soil suggesting that the transport of the two components from the munitions formulations would be governed by dissolution only. On the other hand, both chemicals exhibited some affinity towards WCL, suggesting that the transport of these components in this soil would be influenced by both dissolution and adsorption.

Fate of GIM explosives and their individual components

The batch sorption experiments were also used to evaluate the degradability of the individual components of GIM (HMX and TNT) in DRDC-08 and WCL soils under both sterile and non-sterile conditions. No loss of HMX was observed in either DRDC-08 or WCL soil after three months thus indicating its high stability in soil. TNT appeared to be stable in DRDC-08 soil with only an 8% mass loss after 3 months. However, when the experiment was conducted in WCL soil, TNT had completely disappeared after 23 days, whether the loss happened to be biotic or of chemical origin, resulting in a degradation rate of 0.185 d^{-1}. The amino- derivatives, 2-ADNT and 4-ADNT, were identified in both aqueous and soil fraction, yet final mass balance was very poor.

Exposure of formulations to sunlight in the field may lead to various extents of photodegradation in the solid form or in solution once individual components have leaked into the environment. Irradiation experiments were conducted using artificial sunlight generated from a SolSim solar simulating photoreactor (Luzchem Research, Inc, Canada) with a total irradiance of 590,000 mW m^{-2}. Aqueous solutions of HMX (4.2 mg L^{-1}) or TNT (10.7 mg L^{-1}) in deionized water were irradiated at 25ºC until complete degradation whereas solid dry particles of GIM formulations were irradiated for 48 h in the dry state. At the end of the exposure, the particle was suspended in water in order to quantify the water soluble products identified during the individual component studies (HMX and TNT). A second particle was dissolved in acetonitrile in order to establish mass balances of HMX and TNT. In addition, the pictures of particles were taken prior and after exposure to determine any physical changes.

HMX photodegradation under simulated solar light was fast enough ($k_{HMX\ SS}$ = 0.41 d^{-1}; $t_{1/2\ HMX\ SS}$ = 1.7 d) to allow complete disappearance of the nitroamine in approximately one week (Hawari et al., 2010). The kinetics measured using simulated solar light are more appropriate to predict the HMX photodegradation in the environment and they demonstrate that HMX should

degrade over a week scale if present in the soluble form in surface water. HMX photodegradation with solar light led to the formation of formaldehyde and formic acid through initial denitration followed by ring cleavage as supported by the detection of nitrite, nitrate, ammonia, and 4-nitro-2,4-diazabutanal (NDAB). This product distribution is similar to the one previously determined for HMX photodegradation using irradiation at fixed wavelengths (Monteil-Rivera *et al*., 2008). Mass balances obtained after 7 days showed that carbon mass balance (92%) was higher than the nitrogen one (71%) likely due to the loss of nitrogen in gaseous products such as N_2O or NH_3. TNT photodegradation using the solar simulator gave rate constant estimated at $k_{TNT\ SS} = 3.28\ d^{-1}$ ($t_{1/2\ TNT\ SS} = 0.21\ d$) 10 times higher than the rate measured for HMX photodegradation. TNT photodegradation led to the formation of formaldehyde, formic acid, nitrite, nitrate and ammonia. However, poor mass balances (C: 4.4%; N: 12.4%) were obtained after 72 h when considering only these small end-products suggesting the formation of other products. Analysis of the irradiated aqueous solutions by HPLC/MS revealed the presence of numerous other products of TNT that were identified based on their mass spectra. Most of the identified products were azo or hydrazo dimer forms of TNT, which indicates a tendency of TNT to dimerize, and eventually polymerize further upon exposure to solar light.

Analysis after 48 h-photolysis of formulations in the dry form showed a 19% loss of HMX and a 29% loss of TNT from the initial GIM particle. This result suggests that photodegradation of the formulation components can occur even in the absence of water. None of the small end-products previously identified during the aqueous photolysis of HMX or TNT were detected in aqueous washings of the dry irradiated formulation particles, thus suggesting the occurrence of different reactions in the dry state with gaseous processes being predominant. LC/MS analysis of the aqueous extract of the GIM particle showed most of the azo (and hydrazo) compounds identified in TNT photodegradation experiments along with additional chemicals of higher molecular weights that were not identified. The acetonitrile extracts could not be used for identification of products due to the high concentration of TNT and HMX in these extracts. Comparing microscopic images of GIM before and after photolysis did not reveal significant morphological changes (Figure 6), except for a neat darkening of the orange color of GIM, likely due to the color of TNT photoproducts.

Figure 6: Microscopic photographs of a GIM piece before (left) and after (right) a 48-h photolysis

In conclusion, two potential degradation processes were investigated for the individual water soluble components (HMX and TNT) of the studied explosive GIM formulation. Both chemicals appeared to be stable in non-sterile DRDC-08 soil, but less stable in non-sterile WCL soil, when incubated in the dark. In particular, TNT had completely disappeared after a 3-week incubation in non-sterile WCL soil. Although controls were not performed under sterile conditions in WCL, loss of TNT in this soil likely resulted from biotransformation by indigenous microorganisms. Photolysis conducted under conditions that are representative of natural sunlight was found to be a fast transformation process for both studied chemicals, HMX and TNT. Although photolysis was found to be faster in aqueous media, significant losses of TNT and HMX also occurred when dry solid formulations were exposed to sunlight thus suggesting that photodegradation is a process that will play a major role in the transformation of explosive components of formulation

particles exposed to sunlight. If dissolution experiments are carried out in real enlightened conditions, photolysis will definitely have to be taken into account since it may affect mass balances before the components have even entered into water and soil.

Outdoor Experiments

To complete the understanding of the fate and behavior of the GIM explosive formulation in real environment, Côté and Martel, (2011) from the Institut national de la recherche scientifique (INRS) performed outdoor experiments on GIM explosive. Outdoor dissolution tests were conducted by submitting the ground GIM formulation to natural conditions on glass fritted funnels. The rainwater and melted snow were collected under the fritted funnels, and the dissolved compounds were analyzed. A physical description of the EM and mass balance were performed before and after outdoor weathering. All the water samples were analyzed at INRS and at DRDC Valcartier laboratories. The GIM explosive formulation was ground with a 10-mesh sieve to mimic what would normally be found in training areas as a more realistic situation. One should keep in mind though that grinding the GIM formulations increased its surface of exposure and represents a worst case scenario. The particle size was measured in water with a laser diffraction analysis system (Malvern Mastersizer 2000 from Worcestershire, UK) and gave values between 120 and 600 μm. Pictures of the formulations before and after grinding are shown in Figure 7. Ground GIM particles (10 g) were exposed to weathering during 546 days. The GIM explosive formulation samples were put on the glass fritted funnels on July 8, 2009. By the end of summer 2010, it was decided to let the experiments run for another year. The residues from each sample were weighed, observed, photographed and analysed to draw final conclusions on the effect of their exposure to weathering.

Figure 7: GIM explosive before (left) and after grinding (right)

The tables containing many large glass fritted funnels that were used as the set-up for the outdoor experiments are shown in Figure 8. The use of big amber glass sampling bottles (2.5 L) helped to decrease the number of samples during the infiltration periods and prevented spills during heavy rains. However it did not prevent the bottle to break under freezing conditions in winter. All the bottles did break during the winter and were changed at the end of spring. No water samples were lost because the film in these plastic-coated bottles protected water from spilling.

Figure 8: Outdoor set-up for GIM exposure

Results indicated that in the first 274 days (August 2009 to April 2010), the GIM formulation released 7.0 mg (0.14% of initial mass) of HMX. After 274 days, the behavior of the GIM formulation changed and at the end of the 546–day period, GIM had released a cumulative mass of 38 mg HMX (0.7% of initial mass) which is an increase in dissolution rates. BRI stated that the dissolution of HMX was more or less constant and this is not what INRS observed in its experiment. It is highly possible that photodegradation occurred during the INRS experiment changing the way HMX was made available for dissolution. For TNT, after 274 and 546 days of exposure, 7% and 24% (900 mg) of the initial mass of TNT was dissolved. In its dissolution rates experiments, BRI mentioned that most of the TNT (96%) was dissolved after a year. In the INRS experiment, the GIM samples were not continuously exposed to water and as a result, less TNT came out of the GIM sample in a real outdoor environment. This means that GIM once exposed to natural environment will take a longer time to expose it constituents to receptors and

eventually will have the time to degrade, adsorb and become less toxic. Furthermore, in the INRS experiment, TNT is not fully recovered meaning that degradation and transformation occurred in the glass fritted funnels showing that the fate and behavior may be consistent with our hypothesis of having a greener explosive that leaches TNT derivatives that bind to soil. The ongoing study on the aged GIM sample in soils will answer these questions.

ECOTOXICOLOGICAL EVALUATION OF GIM

To determine if a new explosive formulation such as GIM is green, its toxic effects to relevant target organisms must be evaluated. BRI conducted a tremendous amount of work and a complete description of these ecotoxicological studies can be found in Hawari *et al*. (2011). The main objectives of the ecotoxicological assessments were to conduct terrestrial, aquatic, and benthic ecotoxicity assays and to assess the adverse effects of the GIM formulation as compared to Composition B, which was used as the reference explosive formulation. Direct soil contact toxicity tests included ryegrass seedling emergence and growth inhibition, earthworm lethality, and earthworm avoidance behavior. Benthic toxicity tests using OECD amended artificial sediments included mussel lethality and sub-lethal immunologic response, as well as amphipod crustacean lethality and growth tests. Toxicity of the explosive formulation was also assessed using soil leachate samples by measuring bioluminescence inhibition in the bacteria *Vibrio fischeri* (Microtox assay), and growth inhibition of freshwater algae and duckweed. For the purpose of the present paper, preliminary results and main conclusions using only GIM and Composition B formulations will be described and can be found in Table 2.

Equilibrium studies

As demonstrated earlier, the GIM explosive formulation contains energetic materials covered with a polymer, which makes the energetic substances safer to handle, but which also prevents their dissolution into water or soil when released into the environment. A standardized method was developed for the amendment of formulations to soil without the use of organic solvents, which could alter the configuration of the polymers. Because the polymers may affect the solubility of the energetic constituents, the homogeneity and soil-water equilibrium were determined at nominal concentrations of 10, 100, 1000, and 10,000 mg/kg. Preliminary results indicate that both total extractable and bioavailable HMX were relatively stable and homogeneous over time in all GIM soil treatments. Total extractable TNT was also relatively stable and homogeneous over time at GIM soil treatment concentrations of 1000 and 10,000 mg/kg. At 100 mg/kg GIM soil treatment, both total extractable and bioavailable TNT became relatively stable after 3 days. Considering these data, it was decided to hydrate and equilibrate the GIM soil samples at room temperature during 3 days prior to the initiation of the toxicity tests. The same tests were repeated with Composition B and a 7-day period was chosen to hydrate and equilibrate the soil samples prior the toxicity tests.

Similarly, sediment-water equilibrium and bioavailability studies were conducted prior to the initiation of the benthic toxicity tests using the OECD artificial sediment (OECD, 2004 a and 2004 b). Preliminary results indicate that HMX and TNT concentrations stabilized after 7 days of water contact with the GIM-amended sediment. The same methodology and conditions were

used for the Composition B-amended sediment and an equilibrium period of 7 days was therefore performed for both formulations prior to the introduction of the organisms.

Toxicity of GIM-amended soil leachates to aquatic organisms

The Microtox test measures the inhibition of bioluminescence of the marine bacteria *V. fischeri.* Preliminary data indicate that both GIM- and Composition B-amended soil leachates significantly inhibited the marine bacteria bioluminescence. The EC_{50} values of soil leachates amended with GIM or Composition B at 10,000 mg/kg were similar, *i.e* 2.0 and 2.4 % v/v, respectively. The toxicological values are expressed as soil leachate volume per volume of diluant (salted water).

Leachates of both GIM- and Composition B-amended soil showed significant inhibition of the freshwater algae *P. subcapitata* growth. Both GIM and Composition B soil leachates amended at 10,000 mg/kg had similar toxicities, with EC_{50} values around 1 % v/v. The toxicological values are expressed as soil leachate volume per volume of algal medium. Because TNT was measured in both GIM and Composition B soil leachates, we hypothesized that the toxicity of leachates of amended soil samples observed using the Microtox and algae growth assays is related to the presence of TNT. To test this hypothesis, results of both assays were expressed as the amount of TNT measured in the soil leachates (Hawari *et al*. 2011). Initial data indicated that, for the Microtox test, the toxicity (inhibition of bioluminescence expressed as concentration of TNT) of the samples was slightly lower than the toxicity of pure TNT. For the algae growth assay, both GIM and Composition B curves converged and followed the toxicity of pure TNT dissolved in water. The discrepancy of results between TNT as a pure compound and that contained in the explosive formulation may probably be attributed to the presence of other compounds such as HMX, or RDX.

In the duckweed *Lemna minor* growth inhibition test, GIM and Composition B soil leachates had a high inhibition effect on the *L. minor* growth, with inhibition percentages ranging between 78-97% and 85-98%, respectively. These results are consistent with those measured with the Microtox and the fresh water algae growth inhibition assay.

Toxicity of GIM to soil organisms

The effects of the explosive formulation-amended soil to terrestrial plants were investigated. Seedling emergence of ryegrass in the negative (water) controls was between 92% and 95%, which complies with the quality control requirements. Initial data indicated that seedling emergence EC_{20} and EC_{50} values of GIM and Composition B formulations are 705 and 3782 mg/kg, and 7750 and >10,000 mg/kg, respectively. The calculated EC_{50} values for shoot growth (dry mass), which is a more sensitive toxicity endpoint than seedling emergence, were 736 and 750 mg/kg, respectively. Based on these results, both GIM and Composition B had significant and equivalent toxic effects on ryegrass growth. The toxic effect of GIM and Composition B on terrestrial higher plants could be related to the presence of TNT in both formulations. The total extractable concentrations of TNT were systematically greater in the Composition B-amended soil samples than in the GIM-amended soil samples. However, the toxic effects of both

formulations on ryegrass growth were not significantly different, indicating that the toxicity is rather related to the bioavailable portion of TNT.

The GIM- and Composition B-amended soils at concentrations of 1000 or 10,000 mg/kg soil induced 100% mortality of earthworms. Hence, GIM and Composition B formulations were both lethal to earthworms at nominal concentrations of 1000 mg/kg and above. This effect can again be attributed to the presence of TNT measured in the amended soils at concentrations above 100 mg/kg.

The effects of the explosive formulation-amended soils on earthworm avoidance behaviour showed that there was a significant avoidance response. An avoidance percentage above 60% is considered to be significant. At amended soil concentration of 100 mg/kg, the avoidance behaviour was 7% for GIM and 20% for Composition B. At higher concentrations of 1000 and 10,000 mg/kg, avoidance was 100 % for GIM and 93 and 100% for Composition B, respectively. The EC_{50} avoidance values were 295 mg/kg for GIM and 290 mg/kg for Composition B. In conclusion, significant avoidance response was measured for both GIM and Composition B at formulation concentrations of 1000 mg/kg and above. Once more, toxicity could be related to TNT leaching out of the formulations.

Toxicity of GIM to benthic organisms

The 7-day exposure to GIM- and Composition B-amended sediments indicated that both formulations had deleterious effects on mussel survival. At the 10,000 mg/kg amended sediment treatment, 30% and 50% lethality were measured in GIM- and Composition B-amended sediments, respectively.

The effects of the explosive formulations on mussel phagocytic activity following the 7-day exposure to GIM-amended sediments were not so clear and no significant difference in the hemocyte cellular viability was measured as compared to negative control. However, a significantly higher number of hemolymph cells/mL (cellularity) was measured in the 1000 and 10,000 mg/kg concentrations as compared to negative control. A significant decrease in the phagocytic efficiency (hemocyte cells that have engulfed three latex beads or more) was measured in the negative control and at 10 and 10,000 mg/kg GIM-amended sediments as compared to mussel initial phagocytic efficiency. Following the 7-day exposure to Composition B-amended sediment, no significant effect was measured in mussel phagocytic activity, hemocyte viability and cellularity as compared to negative control.

Results of the amphipod *Hyallela azteca* survival and growth assays indicated that GIM caused 100% mortality at 1000 mg/kg or more. The LC_{50} and growth EC_{50} values for GIM were 402 mg/kg and 255 mg/kg, respectively. Composition B-amended sediments caused similar inhibition of amphipod survival and growth, with LC_{50} and growth EC_{50} values of 495 mg/kg and 514 mg/kg, respectively. Results indicate that both GIM and Composition B had similar deleterious effects on the growth and survival of the amphipod at concentrations of 100 mg/kg and above.

Conclusions of the ecotoxicological evaluation of GIM

To summarize these preliminary ecotoxicological results, GIM and Composition B were highly toxic to the *Vibrio fischeri* marine bacteria (Microtox assay), to the freshwater algae *P.*

subcapitata, and to the freshwater plant *Lemna minor*. Similar results were observed for the terrestrial plant toxicity test, *i.e.* both GIM and Composition B had significant and equivalent toxic effects on ryegrass growth. Earthworm mortality (100%) was observed after the 14-day exposure in the GIM- and Composition B-amended soils at concentrations of 1000 mg/kg and above. Significant avoidance response was measured in earthworms at GIM and Composition B concentrations of 1000 mg/kg and above. Similar results were obtained using the benthic organisms, *i.e.* mussel *Elliptio complanata* and amphipod *Hyallela azteca*. Both GIM and Composition B had deleterious effects on mussel survival as well as on the survival and growth of the *H. Azteca.* No clear effect could be measured using the mussel hemocyte phagocytic activity assay.

The toxic effect of GIM and Composition B appears to be related to the presence of TNT in both formulations at concentrations greater than 260 mg/kg. The concentrations of total extractable TNT were systematically greater in the Composition B-amended soil samples than in the GIM-amended soil samples. However, the toxic effects of both formulations on ryegrass growth, earthworm survival and avoidance response were not significantly different, indicating that the toxicity is rather related to the concentrations of bioavailable TNT, which did not significantly differ in both explosive formulations at 1000 and 10,000 mg/kg soil treatments.

All toxicity tests were conducted with freshly prepared GIM that was exposed directly to the organisms. Because these tests were performed in a closed environment, TNT leached out from the formulations and exerted its toxicity on the test species. Our approach of developing a green explosive containing TNT is based on the fact that TNT is transformed rapidly by microbial activity or by chemical reactions (demonstrated in earlier sections) into derivatives that bind to organic matter of the soil. This is why mass balances are often poor in our experiments. In the real environment of training or firing munitions containing GIM explosive, once GIM is deposited on the soils by UXO cracking, it is believed that TNT contained in the GIM formulation will transform by sunlight or other means into its metabolites that will bind to the soils, becoming non bioavailable and therefore non toxic. Toxicity experiments are currently ongoing with GIM that was aged in soil prior to the initiation of the toxicity tests.

CONCLUSIONS

Copolyurethane thermoplastic elastomers were prepared using glycidyl azide polymers as macromonomers reacted with MDI. It was found that the ETPEs could be dissolved in melted TNT, allowing their incorporation in either Composition B or Octol type explosives in the melt-cast process. This generated a new family of innovative recyclable insensitive melt-cast explosives named "XRT" and "GIM". Recyclability, insensitivity testing, performance evaluation and processing demonstrated that these explosives can be processed in existing melt-cast facilities, be recycled and perform almost with the same energy as that of Composition B. It was found that the best compromise for the energy and the mechanical properties of the insensitive melt-cast XRT explosive was the copolyurethane thermoplastic elastomer ETPE 2000 at 6% weight in the formulation. To produce a green insensitive explosive, HMX was introduced in the formulation instead of RDX, so mixing the ETPE at 9.5% with melted Octol generated upon cooling a greener insensitive explosive named "GIM". Consequently, these ETPEs offer interesting avenues in the production of insensitive explosives.

Insensitive evaluation of the GIM explosive was carried out and bullet impact, sympathetic detonation shaped charge and slow cook off tests were conducted. In addition to this, vacuum stability, impact and friction sensitivity (BAM), density and viscosities of the melted mixes were measured. Furthermore, performance and shock sensitivity tests (gap tests) were also conducted (Table 1). All the insensitivity tests demonstrated that GIM is insensitive to all tests except the shaped charge test that was not passed. Blow-in-place of 105 mm filled with GIM were done in another study where high order detonations were observed with all items blown by one block of C4. These results will soon be available.

For the RIGHTTRAC project, in the thermal aging tests of the XRT and GIM explosives, unacceptable exudation was observed, jeopardizing the chances of GIM explosives to be used as an insensitive explosive. After careful investigation, it was realized that the source of the problem was the ETPE itself. For these formulations, commercially produced ETPEs were used and revealed not ideal for our application. The synthesis of the ETPEs was repeated at DRDC Valcartier at an exact NCO/OH ratio equal to one and this led to a higher molecular weight copolymer with a higher hard segment content. As a result, the aging tests were repeated with new formulations using this latter polymer, and no exudation or at least acceptable exudation was observed.

Environmental evaluation of the GIM explosive was achieved and it was demonstrated that in the GIM products, the ETPE is slowing down the dissolution process of TNT and this phenomenon becomes more important with time since as a result of TNT dissolution, the products are shrinking. This increases the proportion of polymer in the product and its ability to minimize further dissolution and leaching. It was observed by BRI that TNT was almost completely dissolved from GIM in a year in immersed experiments while INRS showed that after 1.5 years of outdoor exposure, only 24% of the TNT was leached out from the formulation.

The toxicity of GIM was tested in soil using earthworms and a terrestrial plant (ryegrass), in soil leachate using aquatic organisms (Microtox, freshwater algae, and aquatic plant *Lemna minor*), and in sediment using benthic organisms (mussel and amphipod *Hyalella azteca*). Preliminary results indicated that the GIM formulation was toxic to all receptors in all toxicity tests, presumably due to the exposure to TNT that leached out from the formulation (Table 2).

As mentioned, the ETPE slows down the dissolution of TNT and in that sense; it reduces the impact on the environment compared to Octol since the concentrations of TNT leaching out of the GIM products are lower over a longer period of time. GIM was developed by DRDC Valcartier as a green explosive, based on the low solubility of HMX and on the fact that TNT should rapidly photo-transform into insoluble dimers and oligomers or bio-transform into amino-derivatives that bind to the soil organic matter. In training scenarios, GIM would eventually be released on the ground, and be exposed to sunlight and microbes. It would thus be interesting to verify if a soil exposed to GIM is still toxic after weathering and aging when most TNT is expected to be transformed and immobilized in soil. Therefore, a new set of experiments has been initiated using a controlled aging and weathering process prior to the initiation of the toxicity assays. Toxicity tests will include terrestrial organisms (earthworms and plants) using GIM weathered and aged in soil, aquatic organisms using soil leachate samples, and benthic amphipod *Hyalella azteca* using sediment samples. These results will be published elsewhere.

Finally, it was demonstrated that GIM explosive has a good performance, almost equivalent to the Comp B, a good chemical stability and is insensitive to most of the tested stimuli. It is easy to prepare in conventional melt-cast facilities, has good mix viscosity and can be used to easily fill projectiles. It was demonstrated that freshly amended GIM was toxic to all target organisms tested. Nonetheless, we still believe that GIM is a greener explosive. Further tests are ongoing to demonstrate that once released into the environment, TNT from GIM will transform and bind to organic matter, and become non toxic, making GIM a viable option as a greener explosive.

ACKNOWLEDGEMENTS

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Table 1 Stability, performance and IM results for XRT and GIM explosives

Test method	XRT 6%	GIM 9.5%
Vacuum Stability	0.8 mL.cm^{-3}	0.8 mL.cm^{-3}
Drop weight impact	20 N	20 N
Friction	360 N	360N
Density	1.65 g.cm^{-3}	1.67 g.cm^{-3}
Viscosity	40 poises	50 poises
Detonation velocity	7689 m.s^{-1}	7726 m.s^{-1}
Detonation pressure	24.2 GPa	24.9 GPa
Plate dent	91.2% Comp B	96% Comp B
Large scale GAP card	167 cards	188 cards

Table 2: Toxicity Results for Soil leachates, soil and benthic microorganisms

Toxicity tests	GIM	Comp B
Leachates from soils amended at 10000 mg/kg		
Microtox: bioluminescence inhibition	2,0% V/V	2,4% V/V
Freshwater algae growth inhibition	1% V/V	1% V/V
Freshwater plant growth inhibition	79-97%	85-98%
Soil organisms		
Ryegrass growth seedling emergence	Ec_{20} 705 mg/kg	Ec_{20} 7750 mg/kg
Ryegrass growth seedling emergence	Ec_{50} 3782 mg/kg	Ec_{50} >10000 mg/kg
Ryegrass shoot growth (dry mass)	Ec_{50} 736 mg/kg	Ec_{50} 750 mg/kg
Earthworm exposed at 1000 and 10000 mg/kg	100% mortality	100% mortality
Earthworm avoidance test at concentrations of		
100 mg/kg	7%	20%
1000 mg/kg	100%	93%
10000 mg/kg	100%	100%
Ec_{50}	295 mg/kg	290 mg/kg
Benthic organisms		
Mussel survival in sediments at 10000 mg/kg	30%	50%
amphipod *Hyallela azteca* survival and growth	Lc_{50} 402 mg/kg	Lc_{50} 495 mg/kg
	Ec_{50} 255 mg/kg	Ec_{50} 255 mg/kg

Figure 1: Bullet impact result on GIM explosive.

Figure 2: Sympathetic detonation set-up.

Figure 3: Shaped charge test set-up.

Figure 4: Oven set-up for the slow cook-off.

Figure 5: Microscopic photographs of a piece of GIM before (left) and after 47 weeks (right) in dripping test

Figure 6: Microscopic photographs of a GIM piece before (left) and after (right) a 48-h photolysis
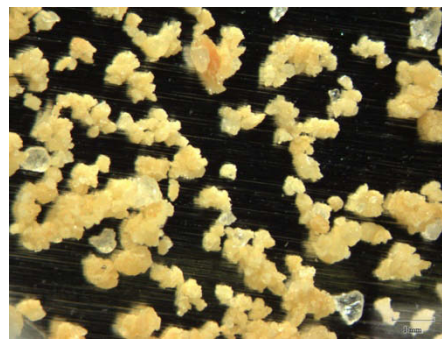

Figure 7: GIM explosive before (left) and after grinding (right)

Figure 8: Outdoor set-up for GIM exposure

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