Review

Synthesis and characterization of a greener insensitive melt cast explosive

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Abstract

For the last two decades, DRDC Valcartier has been involved in the synthesis of energetic thermoplastic elastomers (ETPEs) based on Glycidyl Azide Polymers (GAPs). These ETPEs are copolyurethane thermoplastic elastomers, physically crosslinked rubbery materials that can be dissolved in organic solvent and recycled or can be used as the binder for insensitive melt cast explosives. The mechanical properties of these ETPEs were adjusted to serve as binders in melt cast explosive formulations and give the insensitive character to the formulations. An insensitive explosive named "XRT" for "eXperimental Rubbery TNT" was developed and led directly to the development of a new insensitive recyclable green explosive (GIM). A major project named "RIGHTTRAC" for "Revolutionary Insensitive Green and Healthier Training Technology with Reduced Adverse Contamination" was initiated two years ago and aims at producing a greener weapon. Work was conducted on XRT and GIM explosives to test their performance and sensitivity, their fate and behaviour into the environment, their recycling and value as ingredients to produce a greener munitions based on these concepts. Since ETPEs are recyclable, the ease of recycling and reuse of the ingredients of the new formulations at the end of their life cycle was studied. This paper will describe the syntheses of the ETPEs, the preparation of the XRT and GIM explosives and the results obtained so far describing their properties, insensitive character, recycling, fate and behaviour of formulations and ageing testing.

Keywords : thermoplastic, elastomer, GAP, XRT, GIM

1. Introduction

Nowadays the development of insensitive explosives is of raising importance in Canada because it protects the Canadian Forces and allows their interoperability with other allied Forces. In many countries, efforts are being made to develop new insensitive energetic formulations. In USA, 2,4-dinitroanisole (DNAN) and 3-nitro-1,2,4-triazol-5-one (NTO) are presently the most studied explosives in insensitive melt cast formulations but little is known about their environmental toxicity, fate and behaviour^{1) -4)}. Because of that, other explosives such as : 2,4,6-trinitro-3bromo-anisole (TNBA), picryl propargylether (PIPE), 4,4"dinitro-[3,3': 4',3"-ter (1',2',5'-oxadiazole)] 2'-oxide (DNTF) and 1-methyl-3,5-dinitro-1H-[1,2,4]-triazole (DNMT) are seen as potential TNT replacements while 1,4dinitroglycoluril (DNGU), 2,6-diamino-3,5-dinitropyrazine-1oxide (LLM-105), ditrolone (BNTO), 1,3-dinitro-1,2,4-triazol-5-one (DNTO), 1,3,4-trinitro-1,2,4-triazol-5-one (TNTO), 1,3,3,5,7,7-hexanitrooctahydro-1,5-diazocine (HNDA), bisnitrotriazolone (BNTO), 2-methyl-4,5-dinitro-1,2,3triazole-1-oxide (DNMTO) and, 2,4,6,-tetranitro-2,4,6,8-tetra -azabicyclo [3.3.1] nonane-3,7-dione (TNPDU) are seen as RDX replacements. Of course, there is a lot of work to be conducted before the best green insensitive melt cast explosive formulation is identified.

The development of insensitive explosives can be separated into two families: plastic-bonded or more accurately polymer-bonded cast-cured explosives, which used to dominate the IM explosive development; and more recently, there is an increased interest for insensitive melt cast explosives, mostly based on DNAN and NTO. The great interest for insensitive melt cast explosives is related to the ease of their production since there are many existing industrial melt cast facilities. While plasticbonded explosives (PBXs) were previously utilized in large, high-cost items, such as missiles or bombs, they have found new uses in smaller weapons such as mortars or artillery shells. One good example is the demonstration of the French RDX/HTPB-based HBU88B in the US 120 mm mortar⁵⁾. In addition, 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 that were 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)^{6) - 10)}. Compared to melt cast explosives, the cast cured PBXs are more difficult to process, to recycle, and are generally more costly.

For years, DRDC Valcartier invested efforts at developing insensitive energetic materials. The increased interest of the public towards protecting the environment pressurizes the formulators to make insensitive and greener energetic materials that will be less harmful for the environment. DRDC Valcartier developed energetic thermoplastic elastomers (ETPEs) based mainly on linear glycidyl azide polymer (GAP) to give the insensitive character to the formulations. These energetic thermoplastic elastomers were prepared by reacting GAP macromonomers with 4,4'-methylenebis as (phenylisocyanate)(MDI)¹¹⁾. By doing so, energetic copolyurethane thermoplastic elastomers were obtained and these rubbery materials physically cross-linked matrixes were mixed with secondary explosives and provided the basis for a new generation of insensitive explosives. Many approaches were taken to develop ETPEs and the complete description of GAPs, their synthesis and the ETPEs obtained from them were published^{12), 13)}.

From the very beginning of the project, DRDC Valcartier aimed at developing ETPEs that could melt at 85°C and behave as a GAP-cured system to replace TNT in melt cast formulations. The main problem of incorporating these ETPEs into melt cast insensitive explosive formulations is that the melt cast process is a solvent-less process and once melted; ETPEs would give very high mix viscosities. In addition to that, our ETPEs could not be melted because they decompose before melting. So, according to the present knowledge, it can be said that it was an unachievable goal to replace TNT (a melted organic energetic molecule) in the melt cast process with a melted polymer since it would inevitably result in unacceptable high viscosities, making the processing impossible in conventional melt cast facilities.

The key to produce a melt cast explosive based on theses ETPEs was to realize that melted TNT could act as an organic solvent and was able to dissolve the polymeric matrix to obtain acceptable processing viscosities. Even if TNT is considered toxic, the environmental fate and transport of TNT demonstrated that in the environment, this explosive degrades rapidly by photolysis or biotransformation into 2-, and 4-amino dinitrotoluene and other metabolites that form covalent bonds with organic matter of soils, making it not bioavailable^{14),15)}. This means that TNT, once released in the environment, reacts and cannot reach receptors, making it environmentally friendly when used in live firing activities. This was demonstrated on anti-tank ranges in Canada by Martel et al¹⁶. So, this idea of dissolving ETPE in melted TNT was pursued 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. The nitramine RDX has proven to be both toxic and highly mobile in the environment, while HMX is much less soluble, toxic and mobile. Changing RDX for HMX using Octol instead of Composition B led directly to the development of a new greener insensitive recyclable explosive (GIM). It was demonstrated that the best molecular structure for the ETPE in insensitive explosives was obtained with GAP of molecular weight 2000 g·mol⁻¹ used as the macromonomer^{17),18)}. Since ETPEs are recyclable, they allow an easier disposal and reuse of the formulations at the end of their life cycle. This paper describes the syntheses of these ETPEs, the XRT and greener explosives GIM. The paper will also describe the results of the performance, IM testing such as bullet impact, slow cook-off, sympathetic detonation, shaped charge impact, ageing tests and some preliminary environmental data.

2. Experimental and discussion 2.1 Synthesis

2.1.1 Synthesis of ETPEs

The preparation of ETPE was described earlier^{11),17),19)}. The ETPEs were named based on the molecular weight of their GAP macromonomer and, ETPE prepared from GAP of molecular weight 2000 g·mol⁻¹ was named ETPE 2000. 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 copolyurethane. Having a NCO/OH ratio greater than one results in chemical crosslinking from allophanate and biuret bond formation while a NCO/OH below one results in lower molecular weight and may give unwanted behaviour as it will be described later. Years ago, 3M USA was interested at producing our ETPEs based on GAP prepolymers and is at this moment the only source for these products. For the RIGHTTRAC project, a commercial sample of the ETPE supplied by the 3M Company in Minnesota was used to prepare the GIM explosives that were evaluated. This ETPE sample was prepared using a GAP macromonomer having a molecular weight (Mw) of 2400 g·mol⁻¹.

2.1.2 Synthesis of XRT and GIM explosives

The preparations of XRT explosives were described earlier^{17), 18)}. The first formulations were carried out using a concentration of ETPE 2000 of 10%. 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 mixed for a while and upon cooling, the XRT explosives were isolated. This mixture could be poured on a flat surface to make cookies upon cooling that could be used later in the filling of shells or could be poured directly into shells.

The development of XRT explosives led directly to the preparation of GIM explosives using melted Octol instead of Composition B. HMX is considered more environmentally friendly due to its low solubility and toxicity. Introducing HMX into XRT explosives resulted in the preparation of green insensitive munitions GIM. The preparation and procedures were almost identical but this time, the concentration of the ETPE 2000 was adjusted at 9.5% for 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 a level that allows using melt cast facilities while minimizing the HMX sedimentation. Most efforts were done on the GIM explosive and the following results are related to GIM either than XRT even if they are very similar.

The PBX used for comparison is a Canadian composition called CX-85. The explosive is made of 84.25% HMX and has a hydroxyl terminated polybutadiene (HTPB) binder plasticized with dioctyl adipate (DOA) cured with isophorone diisocyanate (IPDI). The surface agent system is proprietary. The whole formulation is a small modification of compositions presented before²⁰⁾. 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.

2.2 IM test on explosive

IM tests were conducted at DRDC Valcartier mainly on two types of development munitions in 105 mm shell: GIM made with the 3M ETPE sample and PBX (CX-85) formulations made of HTPB cured with IPDI. These tests were also conducted on conventional munitions filled with Composition B for comparison.

Bullet implact, sympathetic detonation, shape charge jet and slow cook-off tests were made and the results were analysed based on a scaling from I to V and overpressure collected according to Annex A of various NATO STANAGs^{21) - 24)}.

In these IM tests, a type I reaction corresponds to the most violent reaction, a supersonic decomposition reaction propagates through the energetic material to produce an intense shock in the surrounding medium e.g. air or water, very rapid plastic deformation of metallic cases followed by extensive fragmentation. All energetic materials are consumed. The effects will include large ground craters for munitions on or close to the ground, holing/plastic flow damage/fragmentation of adjacent metal plates, and blast overpressure damage to nearby structures. Figure 1 shows the size of the fragments following a type I reaction in the bullet impact test of Composition B.

A type II reaction corresponds to the second most



Figure 1 Bullet impact type I result for Composition B explosive.



Figure 2 Type II reaction from one bullet impact of Composition B explosive.

violent type of explosive event. Some, but not all of the energetic material, reacts as in a detonation. An intense shock is formed; some of the case is broken into small fragments; a ground crater can be produced, adjacent metal plates can be damaged as in a detonation, and there will be blast overpressure damage to nearby structures. A partial detonation can also produce large case fragments as in a violent pressure rupture (brittle fracture). The amount of damage, relative to a full detonation, depends on the portion of material that detonates. Figure 2 shows the size of fragments encountered in one of the bullet impact tests for Composition B.

A type III is the third most violent type of explosive event. Ignition and rapid burning of the confined energetic material builds up high local pressures leading to violent pressure rupturing of the confining structure. Metal cases are fragmented (brittle fracture) into large pieces that are often thrown long distances. Unreacted and/or burning energetic material is also thrown about. Air shocks are produced that can cause damage to nearby structures. Fire and smoke hazards will exist. The blast and high velocity fragments can cause minor ground craters and damage (breakup, tearing, gouging) to adjacent metal plates. Blast pressures are lower than for a detonation. Figure 3 shows the fragments resulting from a sympathetic detonation test of the Composition B explosive.



Figure 3 Type III reaction for sympathetic detonation test for Composition B.

A type IV reaction is the fourth most violent type of explosive event. Ignition and burning of the confined energetic materials leads to non-violent pressure release as a result of a low strength case or venting through case closures (leading port/fuze wells, etc.). The case might rupture but does not fragment; closure covers might be expelled, and unburned or burning energetic material might be thrown and spread the fire. Pressure venting can propel an unsecured test item, causing an additional hazard. No blast or significant fragmentation damage to the surroundings; only heat and smoke damage from the burning energetic material. Figure 4 shows an example of type IV reaction encountered during a bullet impact test performed on a single base propellant M1in a 105 mm munition.

A type V reaction is the least violent type of explosive event. The energetic material ignites and burns, nonpropulsively. The case might split open non-violently; the case can melt or weaken sufficiently to allow mild release of combustion gases, or case closures might be dislodged by the internal pressure. Debris stays in the area of the fire, although closures might be thrown up to 15 meters. This debris is not expected to cause fatal wounds to personnel. Finally, some insensitive munitions simply do not react, in these type V cases, a no reaction results is registered in the evaluation of the munitions. This happened with the GIM explosive and also with the PBX munitions.



Figure 4 Type IV reaction in Bullet impact test for gun propellant M1 in a 105 mm.

2.2.1 Bullet impact

For some tests, over pressure sensors were added to the mounting to obtain information on overpressure reaction. The weapon used for these tests was 0.5 cal armour piercing and the bullet velocity was $850 \pm 30 \,\mathrm{ms^{-1}}$ as described in STANAG 4241²¹⁾. The radar antenna was used to measure the bullet velocity. Evaluation of the reactions was done using the air overpressure and mostly by the characterisation of the fragments collected²¹⁾. Composition B presented a type I and II reaction and failed the test while GIM and PBX led to type V reactions and passed the test. Figure 5 showed that the bullet passed through the shell without reaction in the GIM shell.

2.2.2 Sympathetic detonation

During the test, a shell was used as a donor and another was used as an acceptor. Two other empty shells were placed in the assembly for confinement (Figare 6). To evaluate the result, an overpressure sensor was used to measure air pressure. Outcome evaluation was mainly made by characterizing the size of the fragments collected, in accordance with Annex A of STANAG 4396²²⁾. The projectile with white cap, Composition 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 III reactions and passed the test while PBX had no reaction and passed the test.



Figure 5 Bullet impact set-up and GIM result.





Figure 6 Sympathetic detonation set-up and GIM result.

Figure 7 Shape charge test set-up and GIM result.



Figure 8 Oven set-up for the slow cook-off.

2.2.3 Shape charge jet

The test was conducted according to the following setup (Figare 7). When testing, the shape charge was fired and the jet was directed to the shell. The air pressure measurement was performed by overpressure sensors. The result evaluation was carried out mainly by judging the size of fragments collected. In all cases, type I reaction and multiple fragments were obtained and none of the formulations passed the test²³.

2.2.4 Slow cook-off

The test was conducted using an oven where the temperature was measured at the bottom and front, top and rear, top and center of the oven and also in the explosive inside the shell.

The heating procedure of the sample was done as follows: the experiment started at room temperature and the temperature was increased to 100° C in 30 min (150° C·h⁻¹), then, maintained for 90 additional minutes. 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 STANAG 4382^{24} .

Unattended 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 2.5 minutes later. It was visually demonstrated that the burning reaction started into the gases instead of the explosives and this is not desirable. Nevertheless, type V 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 the most current tests. In sympathetic detonation, the PBX behaved in a better way showing no reaction, but the GIM explosive passed the test having a type III 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.

Table 1 Stability and performance results for XR1 and GIM explosives.			
Test method	XRT 6%	GIM 9.5%	Composition B
Vacuum Stability	$0.8mL\cdot g^{-1}$	$0.8\mathrm{mL}{\cdot}\mathrm{g}^{-1}$	$0.1\mathrm{mL}{\cdot}\mathrm{g}^{-1}$
Drop weight impact	20 N·m	20 N·m	5N·m
Friction	360 N	360 N	240 N
Density	1.65 g·cm ^{−3}	$1.67 {\rm ~g}{\cdot}{\rm cm}^{-3}$	$1.68\mathrm{g}\cdot\mathrm{cm}^{-3}$
Viscosity	40 poises	50 poises	3.1 poises
Detonation velocity	$7689\mathrm{m}{\cdot}\mathrm{s}^{-1}$	$7726\mathrm{m}{\cdot}\mathrm{s}^{-1}$	$7885\mathrm{m}{\cdot}\mathrm{s}^{-1}$
Detonation pressure	24.2 GPa	24.9 GPa	26.4 GPa
Plate dent	$0.72 \pm 0.01 \mathrm{cm}$	$0.76 \pm 0.01 \mathrm{cm}$	$0.79\pm0.01\mathrm{cm}$
Large scale GAP card	167 cards	188 cards	217 cards

2.3 Stability and performance evaluation

In addition to the IM tests, XRT and GIM formulations were evaluated by vacuum stability tests, drop weight impact and friction (BAM), density and viscosities of the melted mixes measurements. Furthermore, performance and shock sensitivity tests (gap tests) were also conducted. The test methods and results were published first for XRT in Diaz et al government report¹⁸⁾. Later, GIM was characterized using the same methods.^{25) - 26)}

If one examines Table1, it can be seen that vacuum stability tests showed a maximum gas evolution for XRT and GIM of 0.8 mL·g⁻¹ which under 2 mL·g⁻¹ is considered stable. Drop weight impact 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 test 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% weight (XRT) and Octol mixed with ETPE 2000 at 9.5% weight (GIM) have densities of 1.65 and 1.67 g·cm⁻³, and viscosities of 40 and 50 poises respectively.

Performance evaluation showed that the detonation velocity for XRT 6% is $7689 \,\mathrm{m}\cdot\mathrm{s}^{-1}$ $^{25)}$ and $7726 \,\mathrm{m}\cdot\mathrm{s}^{-1}$ for GIM²⁶). 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 tests confirmed 91.2% Composition B for XRT (the dent depth in steel plates produced by the XRT was 92% of the depth produced by Composition B in the same test set-up) 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, which correspond to shock sensitivities of 3.1 GPa and 2.4 GPa respectively. As a reference, Composition B has 217 cards for this test, or a shock sensitivity of 1.7 GPa. 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, a reduced shock sensitivity compared to current melt cast explosives, that their performance is good and their behaviour in bullet impact tests is excellent ¹⁸⁾.

2.4 Accelerated ageing

Recently, intensive thermal testing was performed on the latest XRT and GIM melt cast formulations according to the method. It was observed that for the ageing test at 70°C for a week, unacceptable exudation of the polymer was observed both visually and by weighing the exudation product²⁷⁾. After examining in detail the exudation products and the starting materials, it was realized that the ETPEs used as one of the ingredients in these formulations were produced commercially and were not synthesized at the precise needed NCO/OH ratio of one. For the producer, it was safer to do the polymerization reaction at a slightly lower NCO/OH ratio than one to ensure that no chemical crosslinking occurred in their batch reactor, but this resulted in a lower molecular weight of the copolymers and also a lower hard segment percentage. Having a lower percentage of hard segments resulted in a softer rubber that has less hydrogen bonds and this allowed the exudation of the material. The synthesis of the ETPEs was repeated at DRDC Valcartier using GAP of M_w 2000 g·mol⁻¹ with an exact NCO/OH ratio of one and this led to a higher molecular weight copolymer with a higher hard segment content. As a result, the ageing tests were repeated and no exudation products or at least a little exudation quantity, judged acceptable, was observed. The exudation products were low molecular weight ETPE copolymers. Conducting the synthesis at a precise NCO/OH ratio of 1 increased the higher molecular weight and lowered the presence of low molecular weight copolymers and as a direct result, almost no exudation was observed.

2.5 Recycling

An important aspect of using thermoplastic elastomers in insensitive explosive formulations is that they allow easy recycling compared to cast-cured PBXs. The most costly ingredient in theXRT and GIM is RDX or HMX. It was demonstrated that the XRT or GIM products can 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^{18), 28)}. The filtrate contained the ETPE and TNT which could be separated using a soxhlet with hot methanol as the extraction solvent. TNT was consequently separated from the ETPE which can be reused¹⁸⁾.

2.6 Environmental fate and behaviour

To understand the environmental fate and behaviour of our insensitive explosives, many experiments are presently under way. Evaluation of the toxicity, dissolution rates in columns and in outdoor set-up experiments where the explosives are exposed to weather conditions are still ongoing. All these results will be presented in a subsequent paper. Preliminary results from column experiments and dripping tests indicated that in the GIM products, the ETPE is slowing down the dissolution process of TNT because it surrounds TNT forbidding the solvent to dissolve the TNT²⁹). This phenomenon becomes more and more important with time because, as a result of TNT dissolution, the entire volume of the products are shrinking and the proportion of ETPE surrounding TNT crystals in these smaller volumes become greater. That increase of the proportion of polymer in the product increases its ability to minimize further dissolution and leaching. Column experiments were conducted using solid formulation in soils. Flow from top to bottom was selected to allow easy introduction and removal of the solid compositions. The dripping tests were conducted using a funnel where the GIM explosive was placed and drops of water were dripped on the sample. Water was collected and analysed for explosives constituents.

Preliminary data on the toxicity of the GIM revealed that when confined with the receptor, the product is toxic because the first product to leach out is TNT³⁰. 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 the GIM products are lower over a longer period of time. In the context of live firing and considering that the TNT concentrations will be lower, the environment may have the ability to do natural attenuation in this case. TNT was chosen as a green ingredient because it has the ability to photo-transform or bio-transform into metabolites that react with organic matter of the soil and becomes non bioavailable and nontoxic. This was not measured by our toxicity experiments so far because the receptors were exposed by direct contact with the pure GIM products. A new set of toxicity experiments will soon be initiated on soils contaminated with GIM previously exposed to sunlight or left to biotransform. It is believed that these GIM contaminated soils allowed to bio or photo transformed will show TNT metabolites fixed to organic matter thus presenting no or less toxicity. This will be described elsewhere.

3. Conclusion

Copolyurethane thermoplastic elastomers were prepared using glycidyl azide polymers as а macromonomer reacted with MDI. The main problem of incorporating these ETPEs into melt cast insensitive explosive formulations was that the melt cast process is a solvent less process and that the ETPEs could not be melted because they decompose before melting. Once it was found that the ETPEs could be dissolved in melted TNT, it allowed their incorporation in either Composition B or Octol type's 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 ETPE 2000. To obtain our best candidates, this copolyurethane thermoplastic elastomer was introduced at 6% weight into Composition B and at 9.5% into Octol to get XRT and GIM explosives. Consequently, these ETPEs offer interesting avenues in the production of insensitive explosives.

In the thermal ageing 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 problems was the ETPEs itself. For these formulations, we used the commercially produced ETPEs that were not synthesized at the exact NCO/OH ratio of one. For the producer, doing the polymerization reaction at a lower NCO/OH ratio was a safety precaution to ensure that no chemical crosslinking occurred in their batch reactor, but this resulted in a lower molecular weight of the copolymers and most importantly in a lower hard segment percentage. The synthesis of the ETPEs was repeated at DRDC Valcartier at an exact NCO /OH ratio of one and this led to a higher molecular weight copolymer with a higher hard segment content. As a result, the ageing tests were repeated with new formulations using this latter polymer and no exudation or acceptable exudation at least was observed. Environmental fate and behaviour experiments revealed interesting data on the toxicity and dissolution of the GIM product, but these experiments are still under way and will be the subject of a subsequent paper.

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