PREPARATION OF ENERGETIC THERMOPLASTIC ELASTOMERS AND THEIR INCORPORATION INTO GREENER INSENSITIVE MELT CAST EXPLOSIVES

Guy Ampleman*, André Marois, Patrick Brousseau, Sonia Thiboutot, Serge Trudel and Pascal Béland
DRDC Valcartier, Québec, Canada
2459 Pie XI Blvd North
Québec, Canada
guy.ampleman@drdc-rddc.gc.ca

ABSTRACT

For years, DRDC Val cartier has been deve loping energe tic the rmoplastic elas tomers (ETPEs) based on linear Glycidyl Azide Poly mers (GAPs). The latest ETPEs developed at DRDC Valcartier are copolyurethane th ermoplastic elastom ers. These copolym ers were so lubilised in melted trin itrotoluene (T NT) and incorpora ted into exp losive formulations to ge t ins ensitive m elt c ast explosives. The dam ping effect from the polymeric ETPEs gave the ins ensitive character and as a res ult, an in sensitive explosive formulation nam ed XRT for eXperim ental Rubbery TNT was developed and later led directly to the deve lopment of the new ins ensitive r ecyclable g reen e xplosive (G IM). Work was conducted on GIM explosives to te st their perform ance and sensitivity, their fate and behaviour into the environment, thei r recycling and their value as ingredients to produce a green weap on based on these con cepts. Since ETPEs are recyclable, the recycling and reuse of the new formulations at the end of their life cy cle was stu died. During the testing of the GIM explosives, ag eing tests revealed that exudation of the commercially produced ETPE occurred over a long period of ti me, jeopardizing the use of these ET PEs in these explosive form ulations. Intense work was conducted on this commercial polymer to understand the issues and solutions were found. This paper will describe the syntheses of the new ETPEs and the solutions proposed to solve the exudation issue. Furtherm ore, the prepara tions of the GIM explosives and results obtained from the IM testing will be discussed.

Topics: Synthesis and characterization, environmental aspects of IM

INTRODUCTION

The work related to the developm ent of new energetic m aterials for m unitions has traditionally been conce ntrated on f inding new molecules that ar e either more powerful and store more energ y than trad itional ones . Nowadays, m ore ef forts ar e m ade at developing less sensitive to unplanned stim uli form ulations that can be used in Insensitive Munitions (IM). DRDC Valcartier h as invested a lot of efforts at developing insensitive munitions over the last two d ecades. To achieve th is goal, energetic thermoplastic elastom ers were developed w ith Glycidyl Az ide Polym ers (GAP) to be introduced as binders in new insensitiv e e xplosives and gun propellant form ulations (Refs. 1-5). Since Canad a uses a larg e percentage of its m unitions during training in our domestic training areas, the environm ental aspects of using live firing weapons at hom e raised is sues that were addressed by the D RDC Valcartier Sus tainable Train ing Programme. Most of the Canadian Forces Bases were characterized for contamination by energetic materials. The analytical chemistry, sample treatment and the sampling strategy were intensely studied and desc ribed in a protocol by Thiboutot et al. (Ref. 6). The fate and behaviour of m unitions con stituents we re also stu died f or the m ost common explosives and energetic m aterials. All this trem endous a mount of work dem onstrated that norm ally f unctioning m unitions only spr ead a very sm all am ount of energetic residues in the environ ment. Most of the contamination in im pact areas com es fr om unexploded ordnances (UXOs) that are cracked open by the detonation of an inco ming round, by incom plete (low-order) detonations , by the destruction of duds or by the corrosion of UXOs. It was also found that RDX has a bad environm ental fate and behaviour, meaning that it does not degrade in soil and, because of its solubility in water, migrates easily to groundwater and off military property.

In addition to this, it w as found that the fi ring position s are im pacted with energ etic residues coming from the incomplete combustion of gun propellant during live firing and from the burning of excess gun pro pellant bags at firing po sitions. To solve the iss ue of the burning of the excess propellant ba gs, a burning table was constructed and implemented in all Canadian bases (Refs. 7, 8). In parallel, most of the weapon platforms

were fired to understand and determine the deposition rates of propellant residues at the firing positions (Ref. 9).

Considering that the Sustainable Training programme demonstrated that the environmental issues come mainly from UXOs, that high order detonations lead to forensic traces of explosives (Ref. 10), also considering the fate and behaviour understanding developed by our main collaborators from the Biotechnology Research Institute (BRI), it was understood that RDX must be avoided. Based on the fact that most environmental impacts are related to UXOs, it was then decided to propose the development of a green weapon based on a zero dud rate munitions containing green explosives and propellants (Ref. 11). This project, named RIGHTTRAC, is a five-year technology demonstration project aiming to show that green and insensitive munitions have better properties than current munitions and that it is feasible to implement a safer weapon solution that would ease the environmental pressure on ranges and training areas, and decrease the health hazards for the users. The approach chosen to develop such green munitions was to develop a self-destruct fuze to avoid UXO production and to replace RDX by HMX in insensitive explosive and propellant formulations.

The GIM insensitive melt cast explosive was chosen to be introduced in the RIGHTTRAC demonstration weapon based on its good insensitive and toxicity results. This insensitive melt cast explosive is produced by dissolving the ETPE in melted Octol and upon cooling, the GIM explosive is isolated. Melted TNT acts as a solvent for the ETPE to dissolve and replacing RDX by HMX gives the green character to the formulation. On the other hand, there is still TNT in the GIM explosive and it is known that TNT is toxic but the environmental fate and transport of TNT was demonstrated by Sheramata and Monteil-Rivera (Refs. 12, 13). They showed 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. 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 Mailloux et al.

(Ref. 14). S o, the idea of di ssolving the ETPE in m elted TNT was studied and resulted first in the developm ent of an inse nsitive explosive nam ed "XRT" f or "eXperim ental Rubbery TNT". This explosive was obtained by m ixing the E TPE with m elted Composition B. The nitramine RDX has proven to be both toxic and highly mobile in the environment, while HM X is m uch less so luble, toxic and mobile. Changing RDX for HMX using octo l in stead of Composition B m ixed with ETPEs led dire ctly to th e development of a new greener insensitive recyclable explosive (GIM).

These energetic therm oplastic elastom ers were prepared by reacting Glycidyl Azide polymers (GAP) of molecular weight 2000 as m acromonomers with 4,4′-methylenebis (phenylisocyanate). By doing so, energetic copolyurethane thermoplastic elastomers were obtained and these rubbery m aterials physical ly cross-linked were dissolved in m elted Octol to get the GIM ex plosives (Refs. 4, 15). Since ETPEs ar e recyclable, they allow an easier dispo sal and reu se of the form ulations at the end of their life cycle. Many approaches were taken to develop ETPEs and the complete description of Glycidyl Azide polymers, their synthesis and the ETPEs obtained from them were described (Refs. 3, 5).

The new GIM exp losive was extensively st udied. The m echanical properties o f the ETPEs and the quantity of ETPE into the formulations were adjusted to optimise the melt cast explosive form ulation visc osity to be suita ble f or pro cessing in ex isting m elt cast facilities at low viscosity and to behave as an insensitive explosive in the IM tests. Work was conducted on GIM explosive to test its perform ance a nd sensitivity, its fate and behaviour into the environm ent, its recycling capability and its tox icity. Some results for the fate and transport of th e GIM explosive can be found in the literature (Ref. 16). Furthermore, a paper describing all these resu lts re lated to the cha racterization of the performance, the IM ch aracter, the fate a nd environm ental behaviour that encom passes dissolution r ate, tr ansport and f ate in soil and in water, and toxicity m easurements is in preparation and will soon be published in International Journal of Energetic Materials and Chemical Propulsion (IJEMCP).

During the testing of the explosive for the RIGHTTRAC project, ag eing testing was conducted at 70ºC for 320 hours and it appeared that a m ixture of polym ers with TNT exudated from the formulations jeopardizing the very exis tence of this explosive. Intensive work was conducted to understand this unforeseen result and it was found that the s tructure of the cop olymers was the pr oblem. Many curing reac tions were done to increase the m olecular weight at the upper lim it and this solved the issue. This paper describes th is work and the f inal c onclusion to get the b est ETPEs that le ad to GIM explosive without showing exudation in the ageing test.

THEORY

In conventional Plastic Bonded eXplosive also named Polymer Bonded Explosive (PBX), inert polymers are reacted with isocyanates to obtain a binder that protects the explosives from shock and other stimuli giving the insensiti ve character to these formulations. This binder is a chem ically crosslinked m atrix produced usually by r eacting a telech elic difunctional hydroxyl term inated polybutadiene (HTPB) with a d iisocyanate and a mixture of triol/triisocyanate to ensure th e chem ical reticulation. In such system s, different mechanical properties of the binde r can be obtained by adju sting the parameters of the curin g reaction and the component c oncentrations, which results in varying the crosslink density of the matrix.

In the GIM explosive, the ETPEs based on GAP 2000 are used as binders to m imic this chemically crosslinked m atrix and get an insensitive recyclable form ulation. Thermoplastic elastom ers are copolym ers of type ABA or AB, where A and B are respectively the hard segm ent and the soft segment (Ref. 17). The hard segm ent is capable of crystallization or association and gives the th ermoplastic behaviour to the copolymer, whereas the soft segm ent gives th e elastomeric behaviour to the copolym er. The therm oplastic behaviour is the result of crystalline dom ain for mation by chain associations due to rev ersible in teractions such as dipole -dipole in teractions, hyd rogen bonding, etc. In the present case, the copolyuret hane thermoplastic elastomers are formed by hydrogen bonding. In practice, at room te mperature, this therm oplastic elastom er behaves lik e a rubber because it is crossli nked in the sam e fashion as a conventional

elastomer, but with reversible physical crosslinks. Since the physical crosslinks are reversible, the ETPEs can be dissolved in melted TNT and could be mixed with the other components and processed. The GIM explosive is obtained upon cooling the formulation.

Polyurethane chemistry is well known and urethane groups are obtained when hydroxyl groups react with isocyanate groups. Water also reacts with isocyanates at a rate similar to secondary hydroxyl groups, yielding carbamic acids which decompose to liberate carbon dioxide in the matrix and form amine groups which are 100 times more reactive than primary hydroxyl groups. In our system, these amine groups react faster than secondary hydroxyl groups with isocyanates, yielding urea groups which introduce rigidity and brittleness to the polyurethanes. Moreover, these urea groups can react with a second isocyanate to give a biuret group, introducing covalent crosslinking between two polymer chains. So eventually, one molecule of water will react with one isocyanate to yield an amine that will react with two isocyanates and introduce chemical crosslinking. This is extremely important in our polymerization system since GAP has secondary hydroxyl groups and water plays an important role in the final structure of the produced copolyurethane thermoplastic elastomer. To obtain linear copolyurethanes without covalent crosslinking, the presence of water must be avoided in order to eliminate these undesirable reactions. This has been stated and emphasized many times but its real importance has been demonstrated only lately in the exudation tests where the final structures of the copolymers had to play an important role in the GIM formulations.

An important aspect of the polyurethane chemistry is the concentration of isocyanates and hydroxyl groups, i.e. the NCO/OH ratio. An excess of isocyanates will lead to covalent crosslinking by allophanate groups formation or biuret formation especially if water is present in a system where secondary hydroxyl groups are involved, as in our case. An excess of hydroxyl groups will lead to incomplete reaction and poor mechanical properties. Thus, the NCO/OH ratio has a direct impact on the molecular weight of the final copolyurethane and on the mechanical properties of this copolymer. Theoretically, when a diol is reacted with a diisocyanate at a precise NCO/OH ratio equal to unity, linear copolyurethane with the highest molecular weight is obtained. To demonstrate that,

Cooper et al. used poly (tet ramethylene oxide), a dihydr oxyl term inated telechelic polyether, as the diol, and polym erized it with MDI (Ref. 17). The y found tha t the copolymer when isolated was a copolyurethane therm oplastic elastomer where the hard segment was the result of hydrogen bonding between the urethane groups. In our polymeric system , GAP is not really di-f unctional having a functionality of 1.6, the hydroxyl groups are secondary hydroxyl groups and it is alm ost i mpossible to produce the ETPE without having som e water present in the system , especially with large quantities of ETPE to produce. All these as pects m ake our polym eric system more complicate to control an d as a result, the m olecular weight and the final structure of the coplyurethane thermoplastic elastomers more difficult to reproduce. N evertheless, it was found that once the equivalent weights of the G AP polymers and the water concentration are known, it is possible to ad just the NCO/OH ratio to get reproducible copolymers with the highest molecular weight.

From an industrial point of view, it is im perative that no chem ical crosslinking takes place in the m ixer avoiding an unwanted situ ation where a rubber is for med in the apparatus. The commercial production of th ese ETPEs using this polym erization system was adjusted to ensu re that no ch emical crosslinking occurred by using a NCO/OH r atio below 1. DRDC Valcartier advised the 3M Co mpany to use a ratio 0.02 below 1 to avoid potential iss ues. It was not realized then th at lo wering th e ratio in this way would have such a negative im pact on the therm al st ability of the copolym ers into the GIM formulations. At that time, we were more concerned by the dissolution of the ETPEs than by its molecular weight and structure.

RESULTS AND DISCUSSION

The GIM explosives w ere prepared by adding the ETPE at a concentration of 9.5% in melted Octol and upon cooling, GIM was isolat ed. The concentration of the ETPE is a key parameter and was adjusted to obtain the best IM properties while keeping the m elt cast viscosity at the lowest le vel possible to allow the use of industrial melt cast facilities while m inimizing the HMX sedim entation. Ma ny IM tests were c onducted w ith this explosive into 105 mm shells. Thes e tests were also conducted with Composition B for

comparison. Bullet impact, sympathetic detonation, shaped charge jet and slow cook-off tests were carried out and the results were analysed based on a scaling from 1 to 5 and overpressure collected according to Annex A of various NATO STANAGs (Refs. 18-21). For the bullet impact test, the weapon used was 0.5 cal armour piercing and the bullet velocity was 850 ± 30 m s^{-1} as described in STANAG 4241 (Ref. 18). Evaluation of the reactions was done using the air overpressure and characterisation of the fragments collected. Composition B presented type 1 and 2 reactions and failed the test while GIM showed a type 5 reaction and passed the test.

For the sympathetic detonation, 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 (Ref. 19). Composition B and GIM had type 3 reactions and passed the test.

For the 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. 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 (Ref. 20). Type 5 reactions were observed for Comp B and GIM that passed the test.

For the shaped charge jet, the test was conducted using a shaped charge that 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 reactions were observed for Comp B and GIM and none of the formulations passed the test described in STANNAG 4526 (Ref. 21). All the IM tests revealed that GIM has insensitive behaviour in the most current tests.

Stability and performance evaluation was also performed. GIM formulations were evaluated by vacuum stability tests (VST), BAM impact and friction sensitivity tests and

measurements of the density and viscosities of the melted mixes. Furthermore, performance and shock sensitivity tests (gap tests) were also conducted. Vacuum stability tests showed a maximum gas evolution of 0.8 mL cm^{-3}. Impact sensitivity tests gave a 20 N m value compared to 10, 7.5 and 5 N m for TNT, Octol and Comp B respectively. The friction sensitivity test gave 360 N compared to 80, 120 and 240 N for TNT, Octol and Comp B respectively. GIM with 9.5% of ETPE has a density of 1.67 g cm^{-3}, and viscosity of 50 poises. The performance test showed that the detonation velocity for GIM is 7726 ms^{-1}. The detonation pressure was calculated at 24.9 GPa for GIM (94% of the value for Comp B). With a value of 0.76 ± 0.01 cm obtained for GIM, the plate dent test confirmed a value equal to 96% of that for Comp B. Large scale gap tests revealed a value of 188 cards for GIM. As a reference, Comp 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 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 (Ref. 15).

For the RIGHTTRAC project, most of the GIM formulations tested were produced using the commercial ETPE 2000 from 3M. Intensive thermal testing was performed on cylinders (3.1 x 26 cm) of these GIM melt cast formulations stored at 70ºC for 320 hours. Unacceptable exudation of a mixture of polymer-TNT (54:46) 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 higher molecular weights for the copolymers were needed to pass the exudation test. As explained earlier, for the commercial producer, it was safer to do the polymerization reaction at a NCO/OH ratio slightly lower 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 2000 with an exact NCO/OH ratio of one and this led to a higher molecular weight copolymer with a higher hard segment content. This was confirmed by viscosity measurements of the GIM mixes at 95ºC. For these measurements, many samples of ETPEs were used to prepare different GIM batches. The commercial sample from 3M, an ETPE sample produced in 2008 and, an older ETPE sample from 2000 were used to prepare GIM and their viscosities were measured at 22.7, 31.3 and 40.5 poises respectively. This means that the laboratory samples had higher molecular weights than the commercial one resulting in higher viscosities. Three additional ETPEs were recently produced using NCO/OH ratios of 0.95, 0.955 and 0.96 trying to push the reaction to its limit, without observing any insoluble sample. These ETPEs were used to produce three GIM candidates but unfortunately, their viscosities at 95ºC are not available at this moment. These three GIM samples were tested at 70ºC for 320 hours and showed respective exudation of 5.4, 4.4 and 1.4 g out of 550 g formulations respectively. As a comparison, the GIM with the 3M, the 2008 and the 2000 ETPEs showed an exudation of 27.2, 17.0 and 10.8 g respectively while pure Octol exudates 1.9 g in the same conditions. This showed that the recent ETPEs have higher molecular weights and as a consequence, little exudation is observed. For the ETPE prepared at a NCO/OH ratio of 0.96, it is becoming difficult to dissolve the polymer in melted Octol showing that the reaction is at its upper limit.

In addition to this, we realized that reproducibility from batch to batch was difficult to achieve between laboratory and pilot scale. It was realized that even with precautions, the water content may vary greatly between lab scale and larger pilot scale. When water is present, it gives chemical crosslinking. At very low concentrations, it helps achieving higher molecular weights but at some points, the polymers become covalently crosslinked to a point where they can no longer be dissolved. Since it is impossible or at least more difficult to completely remove water from pilot scale samples, we tested polymerizations at different water concentrations and it was soon realized that over 300 ppm of water, it is very difficult to get representative ETPE samples. From this point, we decided to fix the water content to 200 ppm. In other words, we dry the prepolymers until a water content

of 200 ppm is reached and we perform the reaction at a NCO/OH ratio of 0.96. This led to reproducible ETPEs and consequently rep roducible GIM that has no or little exudation. So, by controlling the water as a parameter and adjusting the NCO/OH ratio at 0.96, we solved the exudation problems.

Finally, an important as pect of using thermoplastic elastomers in insensitive explosive formulations is that they allow easy recycling compared to cast-cured PBXs because they are soluble in organic solvent. This is why it is important to adjust the N CO/OH ratio to get the highest molecular weight while keeping the sample soluble. If soluble, the ETPEs allow recycling and recuperation of the m ost costly ingredient HMX in the GIM. I t was demonstrated that the GIM products can be di ssolved in ethyl acetate, resulting in the precipitation of the insoluble nitram ines. The ETPE and TNT dissolve easily into ethyl acetate while the nitram ines are insoluble. Upon filtratio n, the nitram ines were easily recovered (99.9%). The analys is and spectroscopy of these recycled nitram ines were identical to the o riginal ing redients, the refore recupe ration and r euse could b e e asily carried out. The filtrate contain ed the ETPE and TNT which could be separated using a soxhlet with hot m ethanol as the extrac tion solvent. Then, TN T was consequently separated from the ETPE (Ref. 15).

CONCLUSION

Copolyurethane thermoplastic elastomers were prepared using Glycidyl Azide polym ers as a macromonomer reacted with MDI. It was found that these ETPEs could be dissolved in m elted TNT and that m ixing the ETPE at 9.5% with melted Oc tol generated upon cooling a gr eener insensitive explosive named GIM. Recyclability, insensitivity testing, performance evaluation and processing demonstrated that this explosive can be processed in existing melt cast f acilities, be recycled and perform almost with the sam e energy as that of Composition B.

Insensitive evaluation of th e GIM explosive was done and bullet im pact, sym pathetic detonation, shaped charge and slow cook off tests were conducted. In addition to this, vacuum stability, BAM im pact and f riction se nsitivity, d ensity and v iscosities of the

melted mixes were measured. Furthermore, performance and shock se nsitivity tests (g ap tests) were also conducted. All the IM tests, except the shaped charge test, dem onstrated that GIM is insensitiv e. Vacuum stability te sts showed a maximum gas evolution of 0.8 mL cm^{-3} while im pact sensitivity te sts gave a 20 N m value. The f riction sensitivity test gave 360 N. It was showed that GIM has a density of 1.67 g c m^{-3}, and a viscosity of 50 poises.

In the therm al ageing tests, GIM explosives demonstrated unacceptable exudation. After careful investigation, it was r ealized that the source of th e problems was the ETPE itself. For the RIGHTTRAC GIM form ulations, we used the commercially produced ETPE and it appeared that the m olecular weight of th is polymer was not optim al. The synthesis of the ETPEs was repeated at DRDC Valcartier at NCO/OH ratios to g et th e high est molecular weights with a higher hard segm ent content. As a result, the ageing tests were repeated with GIM prepared from these new ETPEs and acceptab le exudation was observed. V iscosities at 95ºC of different GIM prepared us ing different ETPEs showed that the lower th e viscosity of the GIM the h igher the exudation will b e. This is n ormal since ETPE with higher m olecular weight wi ll be m ore difficult to exudate and the corresponding viscosity of the GIM will be hi gher. So it was realized that to avoid exudation, higher m olecular weights are need ed while keeping the structure linear meaning the polymers are still soluble. This can be only accomplished with the optimized and controlled NCO/OH ratio. It was also re alized th at even with the sam e NCO/OH ratio, sam ples from laboratory and pilot plan t were giving different ETPEs. W ater was the source of the prob lem and it was decid ed that the prepolymers must be dried until a value of 200 ppm of water is reached and th en the polym erization is perform ed at a NCO/OH ratio of 0.96 leading to reproducible materials. These latter ETPEs lead to GIM with no or little exudation.

Finally, it w as dem onstrated that GIM e xplosive has good perform ance, good chemical stability an d is insens itive to m ost of the tested stim uli. It is easy to prepare in conventional m elt cast facilities, has good m ix vi scosity and can be used to easily fill projectiles.

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