New Polycarbonate-Based Thermoplastic Polyurethane Binder for HMX Based Explosives

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Abstract:

Plastic bonded explosive formulations comprised of HMX are commonly used in expensive precision weapons platforms. Thermoset polyurethanes have been studied extensively as binders for these explosive charges. We chose to examine thermoplastic polyurethanes (TPUs) based on the processing advantages they promise, leading to their application in several established high explosive formulations. For example, aromatic polyester based thermoplastic polyurethanes under the trade name Estanes® have been used in several DOE explosives, including LX-14 (95.5% HMX and 4.4% Estane). Because of the attractive properties of TPUs and the availability of new commercially available polycarbonate polyurethane systems, we have undertaken a study of new HMX-based formulations using new TPUs, mainly derived from polycarbonates. To our knowledge there have been no published energetic material formulations using polycarbonate-based polyurethanes.

The polymers and multiple HMX formulations utilizing the polycarbonate-based thermoplastic polyurethanes (PC-TPU) have been produced and characterized. Commercially available polymers have been characterized by differential scanning calorimetry for glass and melt transition temperatures. Formulations comprised of 95% HMX and 5% binder with different polymers were produced and characterized for small scale sensitivity, pressing density, and processing feasibility. Based on these experiments we found that the isocyanate used to produce the polycarbonate polyurethane is important and believe aliphatic polyurethanes are a viable alternative to traditional thermoset polyurethane in explosive formulations.

Keywords: hmx; polycarbonate thermoplastic polyurethane; aliphatic; aromatic

Introduction

Plastic bonded explosive formulations comprised of HMX are commonly used in expensive precision weapons platforms. Thermoset polyurethanes have been studied extensively as binders for these explosive charges. [1] Thermoplastic polyurethanes (TPUs) were examined based on the processing advantages they promise, leading to their application in several established high explosive formulations. For example, aromatic polyester based thermoplastic polyurethanes under the trade name Estanes[®1] have been used in several DOE explosives, including LX-14 (95.5% HMX and 4.4% Estane). Because of the attractive properties of TPUs and the availability of new, commercially available polycarbonate polyurethane systems, we

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[1] [®] Estane and Pearlstick after a registered trademark of the Lubrizol Corporation. Estane is also known as Pearlstick.

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have researched and herein report on HMX-based formulations using new TPUs, mainly derived from polycarbonates.

Polyurethane Background

Polyurethanes are a family of segmented co-polymers consisting of hard and soft "blocks" with urethane linkages (Figure 1). Polyurethanes can either be thermosets or thermoplastics depending on the composition.
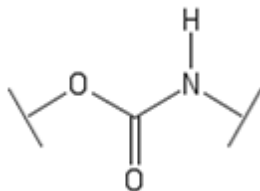

Figure 1.   Urethane linkage

Polyurethanes have three distinct building blocks that dictate their properties: 1) the isocyanate, 2) the polyol, and 3) the chain extender diol (Figure 2, 3). The isocyanate is rigid and will contribute to the hard segment region while the polyol is flexible and contributes to the soft segment region. The chain extender can be either rigid or flexible. [2, 3]
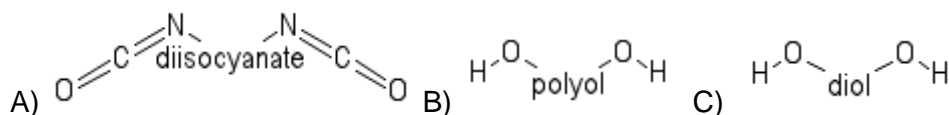
Figure 2.   The components of a polyurethane: A) an isocyanate, B) a polyol, and C) a chain extender diol.
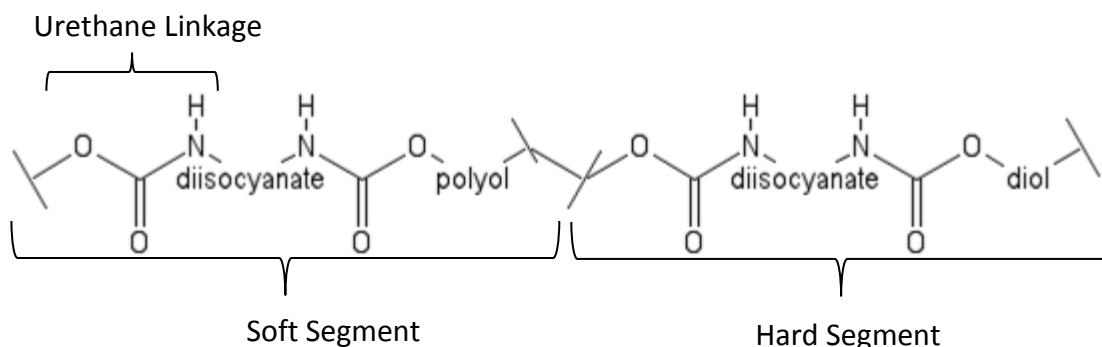
Figure 3.   The repeating units of a polyurethane with 1 of the 4 urethane linkages highlighted along with the soft and hard segments.

Polyurethanes are identified based on the isocyanate and polyols used in their synthesis. Isocyanates are classed as either aromatic or aliphatic (non-aromatic). Aliphatic isocyanates are typically stable to photolysis and have excellent optical clarity and adhesion. Aromatic isocyanates are typically more flexible, stronger, and tougher. [2-4]

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Commercially available polyols used in thermoplastic polyurethanes generally fall into 4 categories: 1) polyester, 2) polyether, 3) polycaprolactone, or 4) polycarbonate. Carbonate polyols are characterized by their excellent hydrolysis and chemical resistance at elevated temperatures and low compression set. [3, 5-10]

Materials

Based on commercial availability and batch sizes, three polycarbonate-based thermoplastic polyurethanes (PC-TPUs) were selected: two aliphatic and one aromatic (Table 1). Estane 5703 is an aromatic polyester-based thermoplastic polyurethane used in LX-14 that has been included as a comparison. The specific material compositions are proprietary.

Table 1: Polycarbonate-based thermoplastic polyurethane properties from vendors

Material	Quadrathane ARC-75A	Quadrathane ALC-75A	ChronoFlex AL 75A-Q	Estane 5703 [now Pearlstick 5703]
Manufacturer	Biomerics	Biomerics	AdvanSource	*Lubrizol*
Type	aromatic polycarbonate	aliphatic polycarbonate	aliphatic polycarbonate	*aromatic polyester*
Durometer (Shore Hardness)	75A	75A	75A	*70A*
Specific Gravity	1.17	1.14	ca 1.10	*1.19*
Ultimate Tensile Strength (psi)	6000	4500	ca 4000	*4500*
Ultimate Elongation (%)	550	500	350–750	*630*

Polymer Characterization

Thermoplastic materials are formed into usable parts in a pressing operation through the application of heat and pressure to melt the binder and form it into the desired shape. In general, the polymer flows and compacts more readily with increased temperature, however, thermal properties and stability of the explosive creates a maximum safe pressing temperature. As an upper limit, HMX goes through a phase transformation at 162 °C [11]. Process capabilities can also place limits. For example, LLNL allows pressing HMX formulations at up to 105 °C with in-die pressures up to 35 ksi.

An indication of the relative processing temperatures required for each binder is provided by consideration of glass transition (Tg) and melt transition (Tm) temperatures for hard and soft segments. Transition temperatures were measured using differential scanning calorimetry (DSC) on 20 mg specimens, sweeping from −80 °C to 205 °C at a rate of 5 °C min^{-1}. All samples were tested as received from the manufacturer, however, it should be noted that the thermal history can impact degree of sample crystallinity, potentially resulting in variations in the measured transition temperatures. [12] The as received condition represents a realistic worst-case scenario for the processability of the material since the final explosive molding powder is not always immediately used and may age prior to pressing. Thermal annealing the samples would have decreased the amount of crystallinity and lowered the transition temperatures. Results are summarized in Table 2.

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Table 2: Transition temperatures for polycarbonate thermoplastic polyurethanes

Type	Polyurethane	Tg (SS)	Tg (HS)	Tm (SS)	Tm (HS)
Aromatic Polycarbonate	Quadrathane ARC-75A	−27.3 °C	not observed	72.4 °C	166.0 °C
Aliphatic Polycarbonate	Quadrathane ALC-75A	−33.3 °C	59.4 °C	118.8 °C	133.3 °C
Aliphatic Polycarbonate	ChronoFlex AL 75-A	−31.4 °C	not observed	68.2 °C	110.5 °C

The primary purpose of DSC testing was to verify that the polymers, in a realistic worst-case condition, would melt at a temperature that could be used in pressing operations. All of the polyurethanes tested had melting points, defined by the hard segments, above 105 °C, the temperature limit for pressing HMX based formulations at LLNL. It should be noted that Estane 5703 exhibits hard segment melting between 150 °C and 200 °C, depending on the thermal history and crystallite content. Furthermore, HMX based formulations with Estane 5703 exhibit acceptable pressing at 105 °C.[12].

Small quantities of 95 wt% HMX and 5 wt% polyurethane were hand mixed and pressed at 35 ksi and 105 °C to determine the maximum achievable density for these formulations. All three formulations reached over 98% of theoretical maximum density (TMD). The results are summarized in Table 3.

Table 3: Percent TMD achieved under maximum LLNL pressing conditions

	Quadrathane ARC-75A	Quadrathane ALC-75A	ChronoFlex AL 75A-Q
Percent theoretical maximum density	98.3%	98.5%	98.3%

To create molding powder for pressing operations, the polymers needed to be dissolved to allow coating of the HMX particles. The major concern with this process was finding a solvent that dissolved the polymers without dissolving significant quantities of HMX. It turns out PC-TPU have great chemical resistance which made it difficult to find a solvent that dissolved the polymers but did not also readily dissolve HMX. A subset of the solvents considered and evaluated along with their HMX solubilities are summarized in Table 4.

Table 4: Solubility of polymer and HMX in various solvents of interest (25 g in 100 mL of solvent)

Solvent System	ChronoFlex AL 75A-Q	Quadrathane ALC-75A	Quadrathane ARC-75A	HMX solubility
Chloroform	Readily dissolves	Readily dissolves	No	0.012 g/100 mL @ 20 °C [13]
Cyclohexanone	Dissolves with minimal heat	Dissolves with minimal heat	Dissolves	1.0 g/ 100 g @ 25 °C [14] 3.06 g/ 100 g @ 30 °C [15]

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50% MEK: 50% Toluene	Dissolves with heat	Dissolves with heat	Dissolves with high heat	1.403/100 g: 0.011/ 100 g @ 30 °C [15]
Benzoflex 9-88 plasticizer + MEK	No	No	Dissolves with heat	Unknown + 1.403/100 g @ 30 °C [15]

Safety Testing

The polyurethanes were verified to be chemically compatible with HMX as determined by gas evolution using the Chemical Reactivity Test (CRT). CRT measures the amount of gasses produced from a 0.25 g specimen after 22 hours at 120 °C. The amount of gas produced by the mixture of HMX and polyurethane is compared to the sum of the gas evolved by the polymer and HMX individually. For all three polyurethanes, the mixture produced less than 0.75 cc g^{-1} of gas beyond the sum of the individual components.

LLNL's standard small-scale safety tests (SSST) were performed to ensure that systems with lower than acceptable margin of safety were identified. Small-scale safety testing is always conducted on samples of candidate formulations before scaling to larger quantities as a best practice. The SSST suite of five tests at LLNL consists: impact (drop hammer), BAM friction, electrostatic sensitivity (ESD), differential scanning calorimetry (DSC), and chemical reactivity (CRT).

The CRT in combination with DSC measurements were used to evaluate both the thermal stability and chemical compatibility of the formulations. In the CRT experiment for a formulation, if the total gas evolved is less than 4.00 cc g^{-1}, the formulation is considered thermally stable for storage. The DSC was used to determine the formulations decomposition temperature with the DSC exotherm onset and peak temperature being reported.

Each of the polyurethanes were dissolved at 7 wt% in cyclohexanone and hand mixed with HMX at a 95:5 wt/wt% and then dried in a 60 °C oven to constant mass after which SSST and pressing studies were performed. A summary of the results is in Table 5 along with LX-14 (95.5 wt% HMX and 4.5 wt% Estane 5703) for comparison.

Table 5: LLNL small scale safety testing on 95 wt% HMX and 5 wt% PC-TPUs

Small Scale Safety Test	Quadrathane ARC-75A	Quadrathane ALC-75A	ChronoFlex AL 75A-Q	*LX-14 (95.5% HMX 4.5% Estane 5703)*
Impact (DH50), cm	66	49	53	*69*
BAM Friction	1/10 @ 36.0 kg	1/10 @ 32.4 kg	1/10 @ 32.5 kg	*0/10 @ 36.0 kg*
Electrostatic sensitivity	0/10 @ 1.0 J @ 510 Ω	0/10 @ 1.0 J @ 510 Ω	0/10 @ 1.0 J @ 510 Ω	*0/10 @ 1.0 J @ 500 Ω*
CRT Total gas release, 22hrs @ 120°C	0.05 cc g^{-1}	0.04 cc g^{-1}	0.10 cc g^{-1}	*0.03 cc g^{-1}*
DSC	Closed: 272.6 °C/278.1 °C (1722)	Closed: 276.6 °C/279.9 °C (1783)	Closed: 279.0 °C/282.1 °C (1605)	*Closed: 276.6 °C/280.7 °C (1565)*

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Onset/Peak Temperature at 5°C, °C (ΔH, J/g)	Pin Hole: 274.0 °C/278.8 °C (1734)	Pin Hole: 278.2 °C/281.4 °C (1741)	Pin Hole: 279.3 °C/282.4 °C (1624)	*Pin Hole: 275.1 °C/279.3 °C (1740)*

Slurry Coating

To determine feasibility at meaningful scales, 50 g batches were slurry coated, in a 1 L vessel with an air driven propeller. The polyurethanes were 7 wt% in cyclohexanone.

The solubility of cyclohexanone in water is 9 g /100 g^{-1} of water at 20 °C but increases with temperature to 78.6 g / 100 g^{-1} of water at 96.6 °C, the boiling point of the azeotrope. [16] Molding powder was successfully formulated by suspending 47.5 g of HMX in 200 mL of water and adding the equivalent of 2.5 g of polyurethane dissolved in cyclohexanone at ambient. An additional 200 mL of water was added to form and solidify the molding powder and the slurry was increased in temperature to reduce the bead size and drive additional cyclohexanone into the water phase.

Using these slurry coating parameters, all three polycarbonate polyurethanes produced molding powder that were similar in size and polymer distribution to one another. However, unlike the Estane formulation LX-14, the molding powders were binder enclosed by HMX rather than the binder-coated HMX (Figure 4-6).
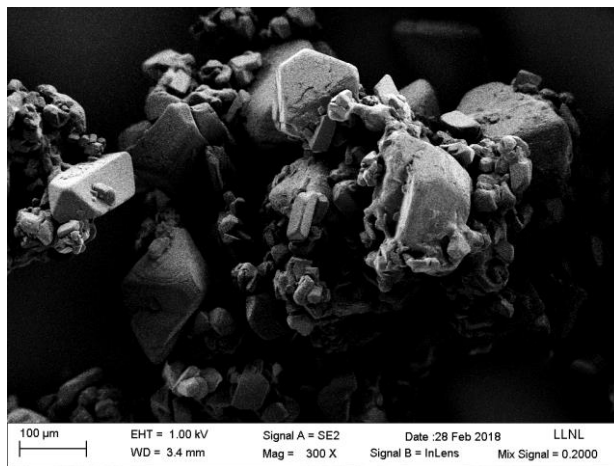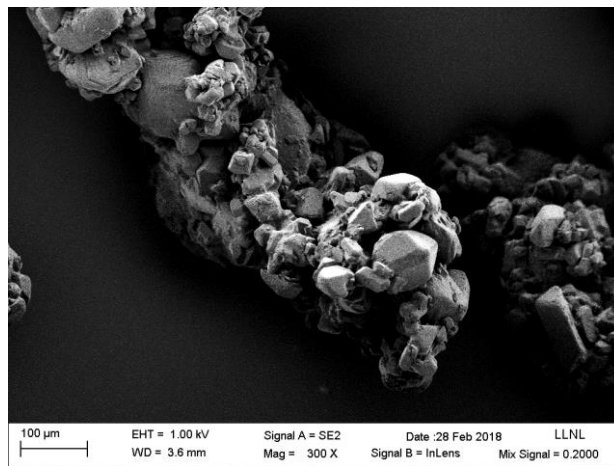

Figure 4. Quardrathane ARC formulated HMX

Figure 5. Quardrathane ALC formulated HMX

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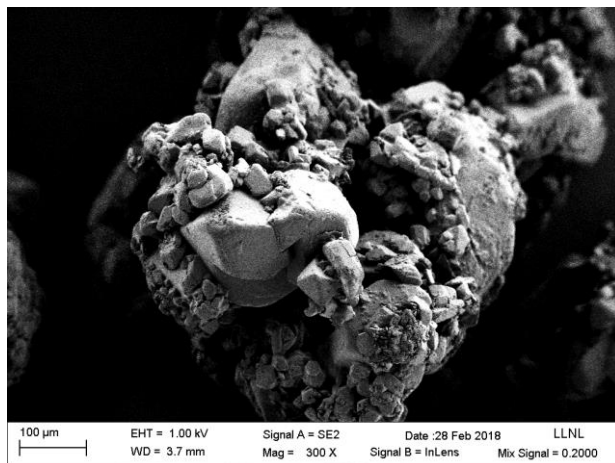robertson37@llnl.gov

Figure 6. ChronoFlex formulated HMX

Discussion

Three commercially available PC-TPUs were selected to determine their feasibility as a binder in an HMX formulation. Two of the PC-TPUs were made with aliphatic isocyanates while the third used an aromatic isocyanate. All three tested as compatible with HMX and had similar safety testing results as LX-14.

Under maximum temperature pressure conditions (105 °C, 35 kpsi), formulations made with each of the three polyurethanes achieved over 98% theoretical maximum density indicating the high melting temperature of the crystalline hard segments is not an issue.

All three polyurethanes formed molding powder using the slurry coating process. Using identical slurry coating parameters, beads were formed that were quite uniform throughout the batch as well as between the different polyurethanes. However, the beads formed were rough and had noticeable crystalline material on the surface as opposed to having a binder rich surface. The greatest difference thus far among the three polycarbonate polyurethanes has been the solubility in a variety of solvents to create a solution for coating HMX. The aliphatic polycarbonate polyurethanes have a variety of solvents they will dissolve in – some more readily than others. The aromatic polycarbonate polyurethane on the other hand, had very few options.

Future Work

These formulations will undergo thermal and explosive characterization. The coeffiecient of thermal expansion will be measured as well as the softening point. The detonation velocity and C-J pressure will be measured using the Disc Acceleration eXperiment (DAX). These tests will offer a more complete picture as to the feasibility of these PC-TPUs in HMX formulations.

Acknowledgements

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