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Energetic silicones: synthesis and characterization of pentaoxadiazole-PDMS copolymers

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Standing at the forefront of energetics research is the exploration of energetic binders. To avoid the traditionally used sensitive explosophores, we present the first reported energetic silicone polymers synthesized from a penta-oxadiazole monomer. These polymers exhibit properties that lie between, or exceed, the thermal properties of inert and commonly used energetic binders.

The design and exploration of new explosives is a unique challenge that requires both increased performance while simultaneously maximizing safety and stability. These materials often bring additional requirements such as high densities, low environmental impact, and mechanical robustness. Unfortunately, as the explosive performance of a material increases, the safety and stability often proportionally decrease. To improve the inherent sensitivity of high explosives (HE) to stimuli (impact, spark, friction, heat, shock), the use of synthetic polymers has been used since the mid-20th century for phlegmatization in the form of plastic/polymer bonded explosives (PBX).[1-3] While these binders increase the overall safety of the PBX formulation, many binders are inert, reducing the overall performance of the HE.[4] To help bridge this safety-performance gap, development of energetic polymers began shortly after in the search of binders that would not only maintain the inherent safety of PBX formulations but also provide a net zero loss (or increase) of energy from the system.[5-7]

Inert binders, such as hydroxyl-terminated polybutadiene (HTPB), styrene-butadiene rubber (SBR), thermoplastic polyacrylate (HyTemp®), and polychlorotrifluoroethylene (Kel-F), have been extensively utilized for the excellent safety and mechanical properties, yet have the undesirable consequence

of reducing the overall energy of the PBX. To combat this problem and input more energy, energetic prepolymers such as GAP, polyBAMO, nitrated HTPB (NHTPB), polyNIMMO, polyvinylnitrate (PVN) (Figure 1) and others have been thoroughly investigated.[8-15] Materials such as polyNIMMO, polyGLYN, and polyvinylnitrate contain nitrate esters ($-ONO_2$) as explosophores incorporated into the repeat unit, resulting in excellent energy release.[4] Additionally, the additional oxygen content provided by these polymers increases the overall density and oxygen balance (OB) of the PBX. While nitrate ester moieties increase the miscibility of these polymers with common oxidizers[16], compared to their azido-based counterparts, they generally have a higher T_g and less desirable mechanical properties. Other well-known energetic polymers such as GAP, polyBAMO and polyAMMO rely on azide (N_3) explosophores for additional energy content. The azide group
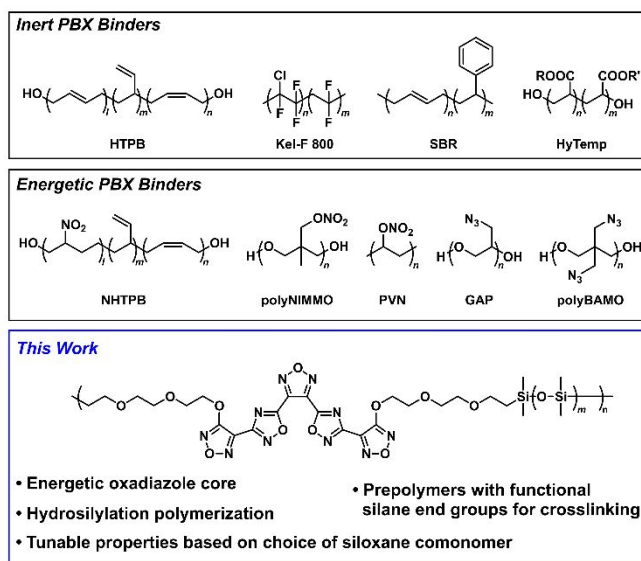
Figure 1 Commonly used inert PBX binders (top), energetic binders (middle), and the material presented in this work (bottom).

provides high nitrogen content and energy via the cleavage of the azide, releasing N_2 and leaving a nitrile group behind. Many energetic polymers are crosslinked in the final stage via urethane linkages due to well-established polymerization conditions of polyurethanes and cheap and commercially available reagents.

However, there are some drawbacks to the use of nitrate ester and azide based energetic polymers as a result of their inherent chemical and thermal instability. Nitrate esters provide increased oxygen content to the system, increasing OB, but often require stabilizers to scavenge degradation products that could lead to exothermic decomposition, resulting in unforeseen and potentially violent reactions.[17, 18] Azides avoid the need for stabilizers but do not contribute any oxygen to the OB and are known for their sensitivity to stimuli.[19]

Due to these polyurethane-based azide/nitrate ester-based polymers being widespread and used throughout the energetics industry, relatively little has been explored in the way of other energetic polymer matrices/scaffolds. This presents an opportunity to explore different areas in the context of energy content and polymer type by using modified CHNO HE precursor materials that already possess energetic properties and high OB while avoiding sensitive explosophores.

Heterocycles comprised mainly of CNO with minimal hydrogen have been established as a way of increasing overall density and energetic content.[20, 21] Reduction in hydrogen content leads to increased OB resulting in higher formation of gaseous products, while increasing nitrogen content has been shown to possess higher heats of reaction.[22] With these properties in mind, oxadiazole heterocycles are attractive targets for incorporation into energetic polymers due to their high heats of formation, high density, and good OB.[24]

Exploration of different base polymers is another tool in the search for desirable mechanical and thermal properties for various application; one such polymer is silicone. Silicone based materials contain potentially advantageous properties, such as low T_g, good mechanical and thermal properties, chemical resistance, tunability and commercially availability. Silicone based PBX's have also shown to have higher heats of detonation and increased insensitivity compared to other inert binders.[23] Despite these enticing characteristics, little to no research into energetic containing silicones as PBX binders has been explored.

Herein, we report on the use of a pentaoxadiazole heterocycle used in the formation of, to the best of our knowledge, the first hydride terminated copolymer containing polydimethylsiloxane (PDMS) with energetic heterocycles. Compound **1** (Figure 2, top) was polymerized with a variety of PDMS monomers of varying chain lengths to investigate the resulting thermal and physical properties.

Model reactions using pentamethyldisiloxane were first used to establish conditions for hydrosilylation of the terminal vinyl ethers in **1**. Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex) showed nearly quantitative conversion of **1** at ambient temperature in toluene within 24 h, as shown by the absence of vinyl peaks in the ^{1}H NMR (Figure 2) and ^{13}C NMR (Figure S2) spectra. FTIR analysis
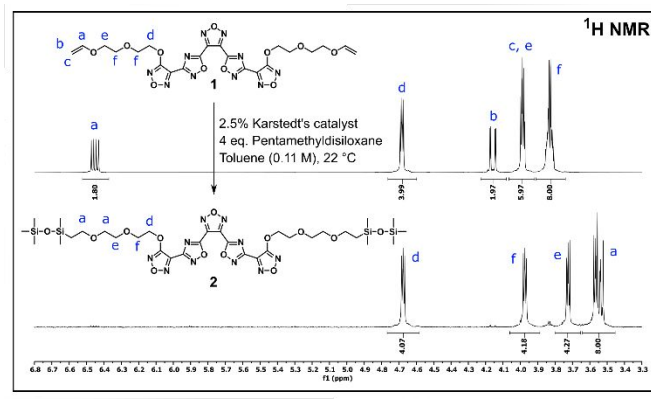
Figure 2 ^{1}H NMR (CDCl₃) of **1** (top) and resulting energetic silicone (bottom) confirming successful hydrosilylation through monitoring of vinyl peaks.

of compounds **2-7** confirmed the absence of vinyl peaks and presence of Si-C and Si-O peaks (Figures S40-45). Although hydrosilylation chemistry is commonly performed at elevated temperatures (60-110 °C),[25-27] we observed undesired side reactions in our experiments at higher temperatures, suggesting **1** may be sensitive to the platinum catalyst under harsher conditions.

Using the established reaction conditions, polymerization with five different sized hydride terminated PDMS (ranging from 1 to 9 repeat units) were performed, with an equimolar ratio of **1** and siloxane comonomers (Figure 3). While **1** is a viscous liquid at room temperature already, these PDMS were chosen due to their low viscosity but also to minimize the non-energetic portion of the polymer as much as possible. After 24 h, 10 eq. of 1,1,3,3-tetramethyldisiloxane was added to the reaction to convert any remaining vinyl functionalities to Si-H moieties, as these polymers were designed to be used as a prepolymer for further hydrosilylation into a crosslinked polymer. Notably, this step did not proceed without a second addition of catalyst. Coupled with the unexpected side reactions at elevated temperatures, this may suggest the oxadiazole core slowly poisons the platinum catalyst. Studies to elucidate the exact mechanism of this interaction are currently underway.

Polymers **3-7** were also characterized via ^{1}H & ^{13}C NMR, DSC, TGA, and IR. As anticipated, ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR and FTIR analysis all confirmed increasing siloxane content as the size of the PDMS comonomer increased (Figures S3-S19, S41-S45). DSC data revealed the thermal characteristics of the materials, summarized in Table 1. High thermal stability was found in **3-7** via their peak decomposition temperatures (T_d) ranging from 334-348 °C (Figure 4A). Materials that exhibit high thermal stability are of substantial interest to several applications, such as space exploration[28] and hypersonic technologies.[29] This is significantly higher than other energetic
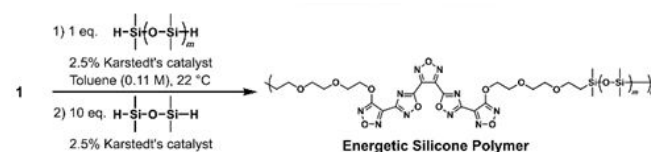
Figure 3 Hydrosilylation reaction scheme used for the synthesis of **3-7**.

polymers, such as GAP and polyBAMO, which have a T_d between 195-230 °C. When comparing the T_d of **1** (302 °C) to the synthesized materials **3-7**, it's clear that the addition of the PDMS chains increases the thermal stability: as the PDMS chain length increases, thermal stability also increases. However, DSC also shows us that as the PDMS contribution to the polymer increase, the energy released at T_d decreases.

Table 1 Thermal data showing glass transition temperature (°C), decomposition temperature (°C), heat of combustion (J/g) and calculated oxygen balance (OB%) for trimer **2**, polymers **3-7** and commercial prepolymers.

Material	T_g (°C)	T_d (°C)	E_c (J/g)	OB (%)
1	N/A	302	2034	-166.9
2	-35	334	623	-130.1
3	-26	335	728	-130.4
4	-35	339	602	-132.3
5	-39	344	376	-135.2
6	-46	346	395	-136.4
7	-48	348	378	-138.3
SBR	-50	432	-230	-313.7
HyTemp	-28	350	-176	-174.7
Kel F-800	30	392	19	-79.8
GAP	-49	230	1696	-121.2
NHTPB	-61	222	1032	-203.8
pBAMO	-37	211	1970	-123.8
pNIMMO	-25	200	1073	-114.2

Typical energetic binders are based on linear carbon-chain polymers, leading to relatively high glass transition temperatures (T_g). To alleviate this problem, the addition of a suitable plasticizer is required to lower the T_g of the binder. While plasticization is a common solution to mitigate a binder's high T_g, this generally leads to other unfavourable results, such as migration of the plasticizer to the surface of the binder. This can lead to void and crack formation, causing the binder to become unpredictable in terms of mechanical and thermal performance.[31] Characterization of the T_g for **3-7** ranged from -26 to -48 °C showing a trend that as the length of the PDMS chain increases, the T_g becomes lower (more negative), possibly removing the need for plasticization depending on the binder application (Figure 4B).

Thermogravimetric analysis was performed on **3-7** revealing onset mass loss between 325-344 °C coinciding with the DSC onset decomposition of the respective polymer, further confirming the high thermal stability of these polymers (Figure 4C). Mass loss ranging from 76-90% were recorded and remained unchanged up to 600 °C. The lack of full decomposition is likely due to the negative OB% in the polymers, resulting in the material not fully converting into gaseous products. This problem is usually addressed during formulation by additional oxygen content being provided by the explosive material used or by the addition of oxidizers.

Comparison of energetic potential was analyzed by examining the decomposition energy (E_c) at the exotherm of T_d (Table 1). Generally, results showed that as the length of the PDMS portion increased, energetic release decreased ranging from 378 – 728 J/g. When compared to inert materials such as HyTemp or SRB (-176 J/g and -230 J/g respectively) and common energetic polymers such as GAP and NHTPB (1696 J/g and 1032 J/g), silicones **3-7** land in-between these energetic bounties, filling a sizable gap in the energetic content of polymers used in PBX formulations.

Another important characteristic to consider is the OB%. This is a metric that indicates to what degree an explosive can be oxidized to form gaseous products, such as CO, CO_2, metal oxides, and others. OB% is calculated with Equation 1

$$OB\% = \frac{-1600}{MW}\left(2x + \frac{y}{2} + m - z\right)$$

where MW = molecular weight, x = number of carbon atoms, y = number of hydrogen atoms, m = number of metal atoms, and z = number of oxygen atoms. Explosive materials tend to approach their maximum strength and brisance potential as OB% approaches zero, however, this also tends to increase their sensitivity.[20] Negative OB% tends to reduce overall energetic potential due to inadequate oxygen presence to fully oxidize the material, resulting in carbon soot, which negatively impacts the pressure-volume work of the detonation. Positive OB% results in more oxygen than is needed for full oxidation during detonation and these materials (such as perchlorate salts) are generally strong oxidizers and used as additives to increase OB%.

Inert binders such as SBR and HyTemp contain very negative OB% (-313.7% and -174.7% respectively), resulting in large amounts of carbon soot during detonation, significantly reducing overall performance of the PBX. Conversely, energetic polymers such as GAP and polyNIMMO display a less negative
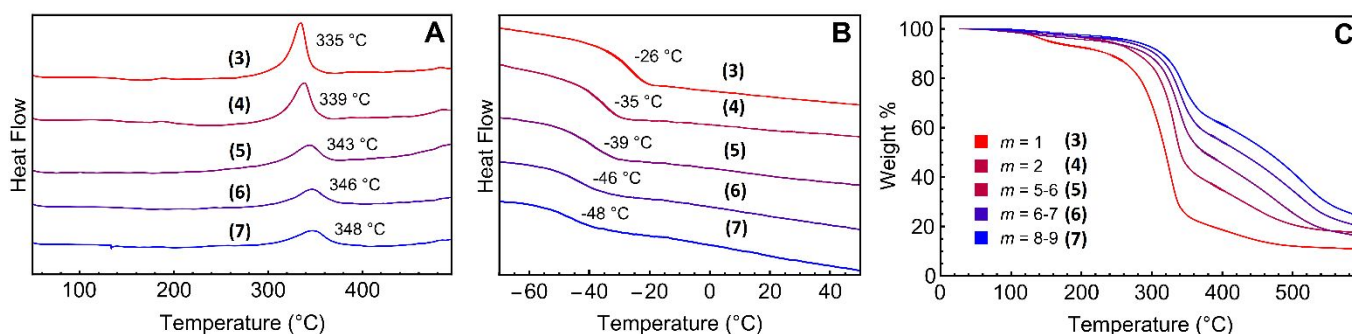
Figure 4 Thermal analysis of polymers **3-7** showing Td (A) and Tg (B) using differential scanning calorimetry and thermogravimetric analysis showing relative mass loss (C).

OB% (-121.2% and -114.2% respectively), increasing their explosive performance as seen by their relative E_c while also increasing their potential sensitivity. Polymers **3-7** display OB% ranging from -130.4% to -138.3% (Table 1), once again, falling between the regime of inert and energetic polymers.

M_w values determined by GPC analysis ranged from around 3 kDa to 15 kDa, increasing with the size of the PDMS comonomer (Table S1). Low molecular weight polymers were targeted with the goal of synthesizing low viscosity oils for use as prepolymers in future formulations or additive manufacturing applications. GPC analysis of **3-7** shown the number average molecular weight (M_n) ranged from 1.9-5.1 kDa and the weight average molecular weight (M_w) ranged from 3.2-15.3 kDa (Table S1). This resulted with the successful synthesis of hydride-terminated low MW polymers that remained a viscous oil under ambient conditions.

With the goal of maximizing energy content and safety parameters while maintaining mechanical and thermal properties, the development of energetic binders has often proved difficult: as one characteristic increases, generally, the others tend to decrease. In this effort, we have developed the first energetic silicone polymers based on the hydrosilylation of the penta-oxadiazole based molecule **1** and PDMS without using sensitive explosophores. Characterization of these materials showed E_c values between 372-728 J/g and peak decomposition temperatures between 334-348 °C. Glass transition temperatures were found between −26 and -48 °C with M_n ranging between 1.9 - 5.1 kDa, resulting in a viscous oil at ambient conditions for all polymers. When these materials were compared to inert and common energetic binders, it was found that these energetic silicones lie between the two regimes. While these materials have shown great promise, future work will be done to incorporate these into formulations used in traditional melt casting of PBX materials but also as HE inks to be used in the additive manufacturing of energetic parts.

Data availability

The data supporting this article have been included in the ESI.

Conflicts of interest

The authors declare that there are no conflicts of interest.

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