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Thermal investigations of nanoaluminum/perfluoropolyether core-shell impregnated composites for structural energetics



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ABSTRACT

An operationally simple blendable approach to producing structural energetic composites loaded with nanoaluminum (n Al) particles coated by perfluoropolyethers (PFPE) yields shape moldable, structurally flexible materials. The epoxide system of poly(ethylene glycol) diglycidyl ether (PEG DGE) and triethylenetetramine (TETA) are partially cured with an energetic blend of n Al/PFPE core-shell particles and mechanically mixed and produce a homogeneous composite material whereby energetic potency is indefinitely shelf stable. The composites are characterized by a suite of thermal techniques using DSC, TGA, and SDT in addition to open flame burn rate and heat of combustion measurements. This composite system may further expand the use of energetic materials with tailorable exothermic properties.

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1. Introduction

The development of novel energetic structural composites is an area of growing interest for both military and commercial applications [1]. Energetic materials are often engineered to be stable and structurally robust yet exothermically decompose under programmable conditions such as at a specific temperature, upon impact, or when exposed to other energy stimuli. Composites are an ideal selection for the design of a structural energetic material because they provide reactive reinforcements in a non reactive host polymer matrix material. Often the reactive reinforcements in these systems are metal fuel oxidizer combinations that undergo an oxidation reduction thermite reaction releasing energy. Advances in the field have generated diverse material platforms ranging from bulk components to fibers [2–8].

In general, energetic materials exothermically ($\Delta H < 0$) and spontaneously ($\Delta G < 0$) react. High explosives detonate at supersonic speeds and propellants and pyrolants react on much

slower time scales [9]. Propellants undergo deflagration reactions at subsonic speeds and pyrolants burn at even slower subsonic speeds (i.e., ~ 10 cm/s). Examples of high explosives include TNT ($C_7H_5N_3O_6$), PETN ($C_5H_8N_4O_{12}$), and HMX ($C_4H_8N_8O_8$) [10]. Gun and rocket propellants like black powder, liquid fuels and oxidizers, and composite fuels are examples of propellants [11]; pyrolants are usually fuel rich and are constituted from metallic or non metallic fuels with inorganic/organic oxidizers or alloys. Related to the interest of this work, the classic example of magnesium polytetrafluoroethylene (PTFE or Teflon[®]) vinylidene fluoride (Viton[®]), commonly referred to as MTV, remains one of the most famous and still widely used metal fluorocarbon based pyrolant formulations [12]. This area of fluorocarbon based oxidizers and metal fuels continues to garner interest and has been consolidated in a recent account [13]. Very recent examples from Pantoya et al. have developed numerous energetic materials based on metallized Teflon[®] formulations [14–18].

Previously, we reported a metallized energetic composite by doping the epoxide system, diethylenetriamine (DETA) polymerized with bisphenol A diglycidylether (BADGE), with a blend of n Al/perfluoropolyether (PFPE, commonly referred to as Fomblin[®]) core-shell (fuel/oxidizer) particulate fillers to yield a structurally rigid material [19]. The resulting epoxide composite could be exothermically decomposed at a specific temperature by changing the loading and composition of the n Al/PFPE blend which was quantified by XRD powder diffraction. PFPEs are well known to decompose at

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lower temperatures in the presence of native metals thereby allowing for the design of an energetic material that would decompose at a prescribed temperature [20–22]. To our knowledge, unlike most fluorocarbon based energetic systems, this was the first blended system to demonstrate the use of a liquid oxidizer (the PFPE) which promotes intimate contact with the metal fuel. Based on our initial findings from this previous research which has expanded to energetic metallized electrospun fibers [23], we were interested in producing a mold shapeable, flexible epoxide system in order to expand the type of materials available for structural energetic use. Elastomeric materials could be highly valuable to the energetic community because rigid materials have limited applicability and use. A flexible, structural energetic component can sustain additional stresses without or before damage to the part as a whole and expands the scope of application. Poly(ethylene glycol) diglycidyl ether (PEG DGE) and triethylenetetramine (TETA) are chosen as starting materials due to their ability to form a flexible, solvent swelled network material. The PFPE Fomblin[®] Y is blended with n Al particles to produce an energetic blend that is then loaded in the PEG DGE/TETA epoxy composite producing a novel structural energetic composite. The use of a PFPE is also employed to take advantage of the hydrophobic properties of PFPEs in hopes of creating a composite that is impermeable to moisture and air, ultimately increasing shelf life. In this study, a new structural energetic composite is fabricated and expanded details of thermal properties and their correlations include thermal decomposition, open flame burn rates, and heat of combustion.

2. Experimental

2.1. Materials

Triethylenetetramine (TETA, 60%), poly(ethylene glycol) diglycidyl ether (PEG DGE, avg. mol wt 500 g/mol), and the perfluoropolyether (PFPE) (Fomblin[®] Y LVAC 25/6, avg. mol wt 3300 g/mol) were all purchased from Sigma Aldrich and were used as received without any further purification. The nanometer sized aluminum (n Al) powder was obtained from the US Army Armament Research, Development, and Engineering Center (ARDEC) and has an average particle size distribution of 80 nm, as determined by TEM from the supplier. The manufacturer found the aluminum to be ca. 70% active as determined by TGA analysis by measuring the mass gain due to oxidation.

2.2. n Al/PFPE core shell blend preparation

A 30 wt% blend of n Al/PFPE is prepared according to the method described in previous studies and is briefly summarized here [19]. Typically prepared in 1 g batches, 30 wt% n Al was mixed with PFPE in a glove box, removed from the inert atmosphere, vortexed for 1 min and then used for composite preparation.

2.3. PEG DGE/TETA epoxy resin preparation

The preparation of composites has been reported previously [19]. Optimized epoxy resin formulations were produced by mixing PEG DGE (3.60 g, 6.84 mmol, 90 wt%) and TETA (0.40 g, 2.74 mmol, 10 wt%). Resulting casted pucks are cured at room temperature on the bench top for 24 h producing an optically transparent, flexible solid.

2.4. PFPE/PEG DGE/TETA composite preparation

The PEG DGE/TETA formulation is allowed to partially cure (A stage cure) in open air at room temperature for 15 h before

adding various loadings of PFPE (5–10 wt%). After addition of the PFPE, the entire mixture is stirred for 5 min and fully cured (B stage cure) in open air at room temperature for an additional 24 h producing a white, homogeneous, flexible solid.

2.5. n Al/PFPE/PEG DGE/TETA composite preparation

PEG DGE/TETA formulation is allowed to partially cure (A stage cure) before adding various loadings of the 30 wt% n Al blended in PFPE (6, 10, and 20 wt% n Al/PFPE loading in epoxy matrix). After addition of n Al/PFPE, the composite is stirred for 5 min and fully cured (B stage cure) in open air at room temperature for 24 h producing a dark gray, flexible composite. *Potential hazard note:* In our studies, the preparation of n Al/PFPE blends and resulting composite formulations showed indefinite shelf stability in open air and during physical handling of the materials. These materials are/should be prepared on small scale batches. However, we stress caution in handling these materials by using the proper personal protection equipment (gloves, safety glasses, and flame retardant clothing). Avoid exposing materials to an open flame, direct heating, or other energy point sources (unless under controlled conditions and by an individual experienced in the art) as these formulations have not been fully tested.

2.6. Thermal characterization

All thermal analysis experiments are performed in nitrogen taken from the head space on a liquid nitrogen tank that first passes through Drierite and all sample sizes are ca. 5–10 mg. TA Universal Analysis 2000 graphical software is used to determine the temperature of all thermal events and calculate remaining amounts of samples.

Differential scanning calorimetry (DSC) was performed on a TA Auto Q20 Instrument. Samples are sealed in aluminum hermetic pans with an empty sealed hermetic pan serving as the reference. Two different heating programs are used to probe different thermal transitions. The first program is used to heat treat as prepared samples which are cooled from room temperature to -80°C and are then heated to 350°C at a rate of $5^{\circ}\text{C}/\text{min}$ in order to report the untreated glass transition (T_{g1}) and cure (T_{cure}) temperatures. The heat treated samples are cycled twice from room temperature to -80°C and heated to 150°C at a rate of $5^{\circ}\text{C}/\text{min}$. On the third cycle, samples are heated to a final temperature of 350°C . Heat treated thermal transitions of T_{g2} , pre ignition reaction (T_{PIR}), and maximum (T_{max}) temperatures are reported on the third cycle.

Thermal gravimetric analysis (TGA) was performed on a TA Q500 instrument at a scan rate of $5^{\circ}\text{C}/\text{min}$. The epoxy formulations are heated in a platinum crucible and heated from room temperature to 900°C . TGA is used to determine decomposition temperatures (T_d) and remaining mass balances/char yields (%) of decomposed samples.

Simultaneous differential thermogravimetric/calorimetry analysis (SDT) was performed on a TA Q600 instrument. Samples are measured into a platinum crucible with an empty platinum crucible serving as the reference. Samples are heated from room temperature to 800°C at a rate of $5^{\circ}\text{C}/\text{min}$.

2.7. Burn rate determination

Quantitative burn tests are performed on all samples to determine burn rates in air. Bulk samples (ca. 150 mg) with dimensions ca. $12\text{ mm} \times 2\text{ mm} \times 8\text{ mm}$ are cut from each fully cured puck. The flame from a propane torch is exposed to the sample held by metal tweezers for 10 s and removed upon which the ignited samples burn until the flame is extinguished leaving

only charred products behind. Timing starts when the flame touches the wedge and is stopped when the flame is fully extinguished. Burn rates are reported as the average of two trials.

2.8. Heat of combustion

Heat of combustion was determined using a Parr Bomb calorimeter. Samples weighing 500 mg were placed in a metal crucible in the Parr 1108 Oxygen Combustion Bomb. The bomb was sealed, filled with 30 atm of pure oxygen, connected to the Parr 2901 Ignition Unit, and placed in a Parr 1341 Oxygen Bomb Calorimeter, comprising of 2 kg distilled water in a bath. The top of the calorimeter houses a stirring device driven by a small motor which circulates the water continuously. A thermocouple inserted in the water bath measured temperature for 60 min of experimentation. The first 6 min were used to let the water bath attain thermal equilibrium then the sample in the calorimeter was ignited by connecting the ignition unit to a voltage source. The thermocouple recorded about 35,000 temperature measurements at different instances during combustion. These values were then used to calculate the heats of combustion of the samples according to the ASTM standard [24].

3. Results and discussion

3.1. Composite fabrication

In order to make a structural energetic material, energetic blends of n Al/PFPE core shell particles were incorporated into a cured PEG DGE/TETA epoxide matrix. Previous experiments using DSC determined that the optimum energy output stoichiometric ratio is 70 wt% PFPE and 30 wt% n Al fuel [19]. Varying concentrations of n Al/PFPE were added after 12 h to partially cured (A stage) PEG DGE/TETA mixtures, mechanically stirred by hand, and allowed to cure for an additional 24 h (final B stage cure). It was found that additions of more than 20 wt% n Al/PFPE could not be achieved as the material would not homogeneously cure into a fully cured composite. Control composites were prepared with epoxide resins loaded with PFPE only (no n Al); loadings of >10 wt % PFPE would not fully cure. Epoxide resins loaded with n Al only (no PFPE) could only be loaded with up to 5 wt% n Al to yield homogeneous fully cured materials.

3.2. Composite thermal analysis

Complete thermal analysis including thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and simultaneous DSC TGA (SDT) was performed on composites, and selected properties are shown in Table 1. For DSC analysis,

composite samples underwent two different heating treatments, which are referred to henceforth as untreated and heat treated cycles. A comparison of the DSC traces of the same composite loaded with 10 wt% n Al/PFPE that has undergone either untreated or heat treated cycles can be seen in Fig. 2. Untreated samples were cooled from room temperature to 80 °C then heated to a final temperature of 350 °C. Under these conditions, the control epoxide showed a glass transition temperature (T_{g1}) of 45 °C. The T_{g1} value does not significantly change upon addition of PFPE, n Al, or the n Al/PFPE blend at various loadings to the control epoxide matrix. There is a noticeable event that is slightly exothermic at approximately 138 °C in all untreated samples. This is a final B stage cure (T_{cure}) that undergoes full network formation via unreacted epoxide. Although insoluble, cured formulations were found fusible (e.g., swelled) after soaking for 1 h in organic solvents toluene and dichloromethane, fluorinated solvents such as hexafluorobenzene and Fluorinert™ (FC 75), and deionized water. Heat treated samples were cycled twice from 80 °C to 150 °C. On the third cycle, samples were heated to a final temperature of 350 °C. After one heat treatment cycle, the glass transition temperature of the control increasingly shifts by ca. 10 °C to 55 °C (T_{g2}), and T_{cure} is no longer evident. This trend is apparent for all epoxy resins doped with PFPE and composites loaded with n Al/PFPE.

As seen in Fig. 2, there is a small exothermic transition at 194 °C. This is a pre ignition reaction (PIR) similar to the one observed by Pantoya and Dean in n Al/Teflon thermite based reactions [14]. PIR exotherms were detectable for blended formulations of n Al with PFPE, but this is the first time we detected a PIR after loading the blend into an epoxy matrix [19]. This PIR is exothermic due to the generation of a meta stable C Al F species via a Grignard like reaction (C F + Al) of the PFPE (C F source, see structure Fig. 1) with the surface of the aluminum, as suggested for PIR reactions of MTV [9,12]. The T_{PIR} for the samples with 6 wt% n Al/PFPE occurred at 208 °C, a higher temperature than T_{PIR} for the 10 wt% blend. For samples with 20 wt% n Al/PFPE, the T_{PIR} is expected to follow this trend and occur at a temperature above 208 °C. However, as the loading of the n Al/PFPE blend is increased, the maximum exothermic event T_{max} (vide infra) also shifts, but to lower temperatures. For the composite loaded with 20 wt% n Al/PFPE, T_{max} occurs at 208 °C. T_{max} is a broad peak at the highest loading (refer to black plot in Fig. 3) and due to this wide breadth T_{PIR} presumably overlaps with the main exothermic event making it indistinguishable. It is likely that the PIR still occurs at higher loadings; however, under current experimental conditions (DSC scan rate of 5 °C/min) we are unable to resolve the two events.

For the control epoxy, a maximum exothermic event (T_{max}) occurs at 272 °C in both untreated and heat treated scans. This maximum exothermic event correlates with the formation of the

Table 1
Summary of thermal data of various epoxy resins and composites.

Epoxy (wt%)	n-Al (wt%)	PFPE (wt%)	T_{g1}^a (°C)	T_{cure}^a (°C)	T_{g2}^b (°C)	T_{PIR}^b (°C)	T_{max}^b (°C)	T_d^c (°C)	Mass balance ^d (wt%)
100	0	0	−45	137	−35	–	272	279	3 ^e
95	0	5	−37	139	−33	–	272	275	3 ^e
90	0	10	−45	140	−35	–	271	279	3 ^e
95	5	0	−41	138	−32	–	263	274	7
94	2	4	−44	137	−33	208	270	278	3
90	3	7	−42	138	−31	194	252	276	4
80	6	14	−45	137	−32	–	241	270	9

^a Untreated DSC (5 °C/min) in nitrogen.

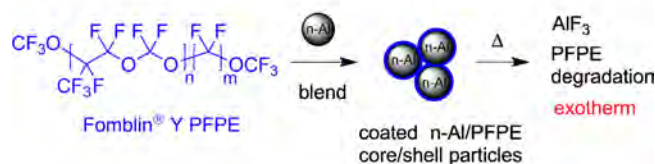
^b Heat treated DSC (5 °C/min) in nitrogen recorded on the third heating cycle.

^c TGA (5 °C/min) in nitrogen.

^d Residual mass balance recorded after 500 °C using TGA.

^e For control epoxy resin, no n-Al or PFPE, 3 wt% carbon char was observed at 800 °C.

Energetic n-Al/PFPE core/shell formulation



Energetic n-Al/PFPE core/shell epoxy composite formulation

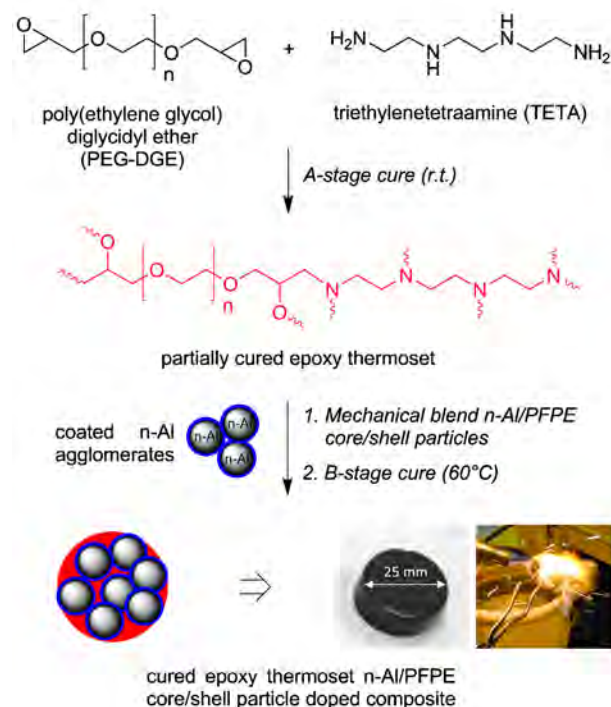


Fig. 1. Schematic depicting the fabrication of structural energetic composites. Top scheme: preparation of energetic formulation of core-shell n-Al/PFPE particles. Bottom scheme: fabrication of metallized composite using n-Al/PFPE particles mechanically blended into a partially-cured epoxy matrix followed by final heat treated cure.

thermodynamically favorable species AlF₃, according to the scheme presented in Fig. 1, and as observed and described in detail in previous studies by our group [19]. Addition of 5–10 wt% PFPE does not shift the location of this exothermic event. However, epoxy resins loaded with n-Al/PFPE shifted in $T_{\max}$ to a lower temperature. The largest shift in $T_{\max}$ occurs for the PEG-DEG/TETA composite loaded with 20 wt% n-Al/PFPE, where $T_{\max}$ is observed at 241 °C (31 °C lower than $T_{\max}$ of the control resin). Fig. 3 shows a close up of $T_{\max}$ for the control epoxy, the composite loaded with 20 wt% n-Al/PFPE blend and an epoxy resin with 5 wt% n-Al only (no PFPE). The exotherm has clearly shifted from the control trace (red trace) to a lower temperature after addition of the energetic blend (black trace) due to metal catalyzed accelerated decomposition of the epoxy matrix. This is consistent with previous experiments of BADGE/DETA epoxides loaded with the metallized energetic blend of n-Al/PFPE [19].

Promptly after the maximum exothermic event, decomposition of epoxy matrix (T_d) occurs as observed by DSC and further reported from TGA (vide infra). In fact, decomposition of the matrix nearly overlaps with $T_{\max}$. This decomposition event is evident in Fig. 3 by an abrupt response from signal output. A representative

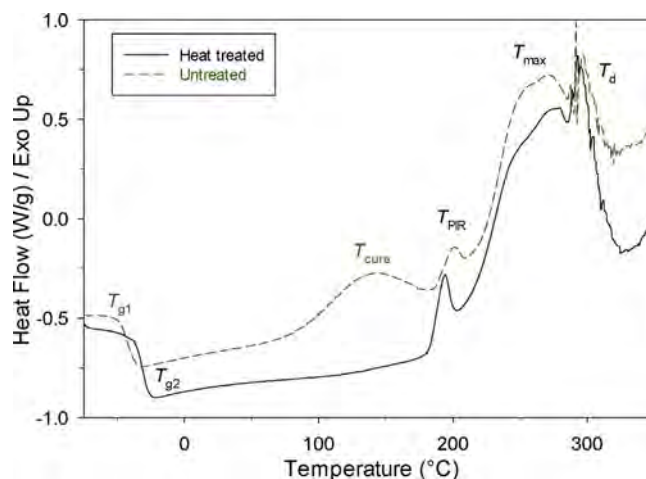


Fig. 2. DSC traces of a heat treated (solid line) and untreated (green dashes) epoxide loaded with 10 wt% n-Al/PFPE. The values of labeled exothermic events are reported in Table 1 (refer to the text for detailed discussion describing events). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

SDT plot of an epoxide loaded with 6 wt% n-Al/PFPE is shown in Fig. 4. In this sample, $T_{\max}$ occurs at 270 °C, and T_d occurs at 278 °C. The values $T_{\max}$ and T_d are listed in Table 1 for all samples. Enthalpies of reaction (ΔH) are generally measured by integrating the areas of exothermic peaks; however, because $T_{\max}$ and T_d overlap, ΔH cannot be accurately determined. Further insight into thermal properties will be expanded with heat of combustion (ΔH_c) analysis in the subsequent section of this report.

The control epoxide decomposes at 279 °C, and the decomposition temperature does not significantly change after addition of any filler. A TGA plot of the decomposition of the control epoxide and a composite loaded with 20 wt% n-Al/PFPE is shown in Fig. 5. After decomposition, the control epoxide has a carbon char yield of 3 wt%. Addition of PFPE does not affect the char yield as PFPEs are well known to decompose into traceless gases [21]. However, upon addition of n-Al/PFPE, the mass balance increases. This increase in char yield is expected due to the remaining weight of the unreacted aluminum and oxidized by products (e.g., aluminum fluoride, aluminum oxide, or aluminum carbide) which correlates well to

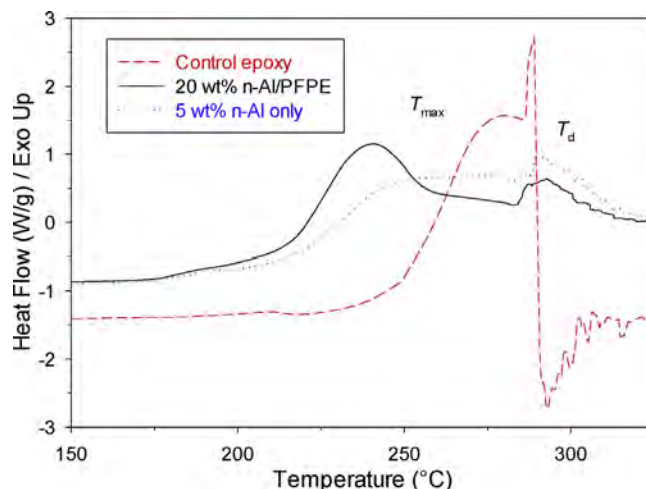


Fig. 3. DSC of the control epoxide without any dopants (red dashes), the epoxide composite loaded with 20 wt% n-Al/PFPE (black solid line), and the epoxide resin loaded with 5 wt% n-Al only, no PFPE (blue dots). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

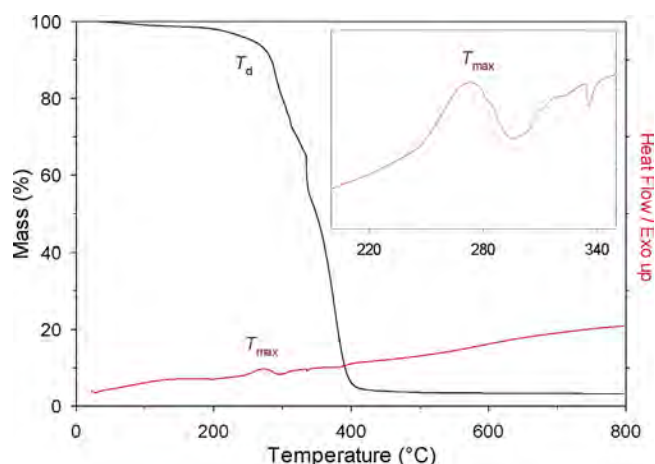


Fig. 4. SDT of an epoxide loaded with 6 wt% n-Al/PFPE. The TGA trace is shown in black and the DSC trace is shown in red. The insert is an expanded view of the exotherm of the DSC trace. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the loaded weights during composite fabrication and post combustion analysis which as been previously studied on rigid epoxide systems [19].

3.3. Composite burn rate analysis

The control epoxy resin and composite samples were ignited, and the time for each to completely burn until the flame was extinguished, and only charred products remained was recorded. Burn rates are calculated and presented in Table 2. It takes the most time to burn the control epoxide sample thereby giving it the slowest burn rate of 0.9 mm/s, which is, presumably, associated with degradation and charring of the hydrocarbon matrix. Addition of PFPE decreases the overall burn time, and therefore, increases the burn rate, as expected since PFPEs are known as excellent heat dissipating fluids. Addition of n Al (no PFPE) greatly increases the burn rate to 5.2 mm/s. This can be attributed to localization of heat in the metal particles followed by a secondary transfer of heat to the matrix thereby decreasing the overall time required for degradation of the sample. Interestingly, upon addition of the n Al/PFPE blends to the epoxy composite, a slight increase in burn rate is recorded for lower loadings, but a turnover is observed and burn

Table 2

Burn rate and heat of combustion (ΔH_c) values of control epoxy and doped epoxy samples with different loadings of n-Al and PFPE.

Epoxy (wt%)	n-Al (wt%)	PFPE (wt%)	Burn rate (mm/s)	ΔH_c exp (kJ/g)	ΔH_c est (kJ/g)
100	0	0	0.9	26.0	26.0
95	0	5	2.8	–	25.3
90	0	10	3.7	24.9	24.7
95	5	0	5.2	25.8	25.8
94	2	4	5.8	25.4	25.4
90	3	7	4.0	25.0	26.0
80	6	14	1.9	23.6	23.6

rates decrease at higher loadings (compare 10 wt% n Al/PFPE with the 20 wt% formulation). This observation is explained after bomb calorimetry results are subsequently presented.

3.4. Composite heat of combustion

Heat of combustion (ΔH_c exp) measured using the Parr Bomb calorimeter is given in Table 2. Since the Al, PFPE and epoxy are all combustible in the oxygen saturated environment of the calorimeter, all burn completely during the heat of combustion measurement experiments. In order to compare ΔH_c measurements to theoretical predictions, an estimate of the heats of combustion for each sample was made based on the heats of combustion of individual reactants using Eq. (1).

$$\Delta H_c = [\text{wt\% active Al} \times \Delta H_{\text{Al}}] + [\text{wt\% PFPE} \times \Delta H_{\text{PFPE}}] + [\text{wt\% epoxy} \times \Delta H_{\text{epoxy}}] \quad (1)$$

The wt% active Al is equal to $0.7 \times \text{wt\% n Al}$ for each sample, based on alumina concentration information from the manufacturer. In Eq. (1), ΔH_{PFPE} is the heat of combustion of PFPE (12.78 kJ/g) [25], ΔH_{Al} is the heat of combustion of n Al (31.05 kJ/g) [26], and ΔH_{epoxy} is the heat of combustion of the epoxy which was found experimentally to be 26.00 kJ/kg. Table 2 shows that the measured and estimated heat of combustion values are very close, suggesting complete oxidation for all samples tested in the calorimeter.

The control epoxy has the highest heat of combustion of 26 kJ/g. Adding 5 wt% n Al decreases this value very slightly to 25.8 kJ/g. Adding 10 wt% PFPE to the epoxy resin decreases ΔH_c to 24.9 kJ/g. The ΔH_{PFPE} is significantly lower than that of n Al or the epoxy resin, which may explain the overall decrease in ΔH_c when PFPE concentration is increased.

The burn rates for the composites are estimated based on the time taken for a fixed sample volume to burn completely. This implies that samples with longer burn times have slower burn rates and vice versa. Heat of combustion and burn rate do not follow the same trend. Despite the potential to generate the most chemical energy, the sample with 5 wt% n Al (no PFPE coating) has a slightly slower burn rate than the sample with 2 wt% n Al/4 wt% PFPE (compare entries in Table 2). The calorimeter has an oxygen rich environment, and therefore, the n Al in the sample with 5 wt% n Al has ample supply of oxygen and will undergo complete combustion. During real time burning, however, since these n Al particles are homogeneously distributed within the epoxy matrix, they have limited access to ample oxygen that may result in slightly more time for complete oxidation. On the other hand, for samples with 2 wt% n Al/4 wt% PFPE, the n Al particles are coated by the PFPE oxidizer which makes their complete combustion more likely. The sample with 2 wt% n Al/4 wt% PFPE shows the fastest burn rate because n Al particles are encased in a PFPE oxidizer shell providing more complete oxidation of n Al.

At high concentrations of n Al/PFPE, the heats of combustion and burn rates decrease because the thermal properties of PFPE appear to diminish the heat of combustion. There is a balance

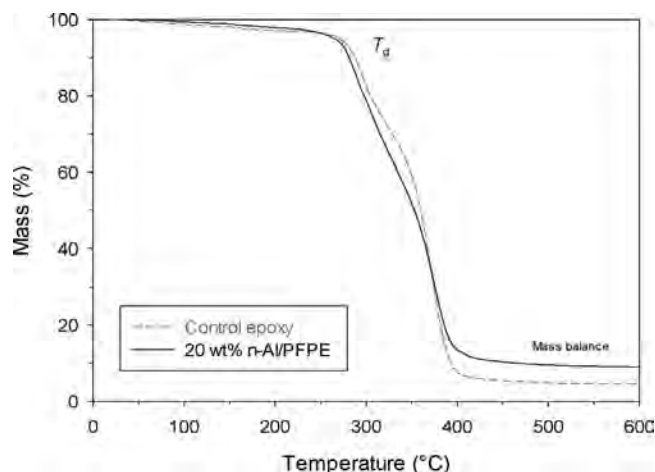


Fig. 5. TGA of the control epoxide without any dopants (red dashes) and the epoxide resin loaded with 20 wt% n-Al/PFPE (black solid line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

between the energy resulting from Al oxidation and the thermal chemical properties associated with PFPE that reduce the overall energy available from reaction (Table 2). The higher concentrations of n Al/PFPE diminish the ΔH_c ; and therefore, slow the burn rate. The higher concentrations PFPE may be responsible for the steadily decreasing ΔH_c and burn rates beyond the 2 wt% n Al/4 wt% PFPE concentration.

4. Conclusions

This work reports the preparation of a PEG DGE/TETA epoxy based composite entrained with a metastable PFPE coated n Al powder formulation reactive upon thermal ignition. Loadings up to 20 wt% n Al/PFPE can be successfully incorporated into the host matrix and still yield a fully curable, flexible material. Thermal studies conclude that the main exothermic event overlaps with degradation of the matrix epoxy; however, it is possible to distinguish a distinct shift in the exotherm to lower temperatures upon increased loadings of the energetic n Al/PFPE blend. Glass transition temperatures of resulting composites do not shift from the control epoxide sample, nor do decomposition temperatures as measured by DSC and TGA, respectively. Burn tests reveal a faster burn rate for the n Al/PFPE loaded composites when compared to epoxides loaded with only n Al or PFPE. Heat of combustion measurements suggests that n Al/PFPE blends possess greater oxygen diffusivity such that reaction propagation is more easily facilitated despite possessing an overall reduced heat of combustion compared with the control epoxy. There is a balance between PFPE concentration that inhibits energy generation and increased energy propagation and increased aluminum reactivity resulting from the PFPE coating. This metalized epoxy composite system is a slow burning pyrolant packaged in a flexible, moldable material that can be machined post cure to any desirable shape thereby expanding the possible energetic applications available for use.

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