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Fabrication, Characterization, and Energetic Properties of Metallized Fibers

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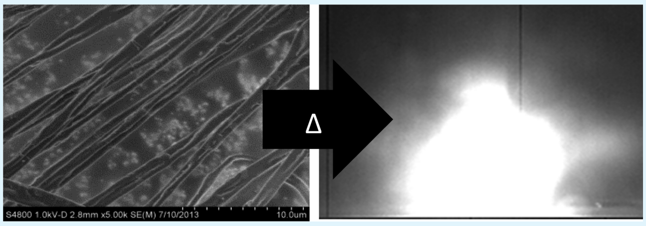

ABSTRACT: Polystyrene fibers loaded with an energetic blend of nanoaluminum (n-Al) and perfluoropolyether (PFPE) were successfully fabricated via electrospinning producing nanothermite fabrics. Fibers were generated with loadings up to 17 wt % n-Al/PFPE incorporated into the fiber. Microscopy analysis by SEM and TEM confirm a uniform dispersion of PFPE treated n-Al on the outside and inside of the fibers. Metallized fibers were thermally active upon immediate ignition from a controlled flame source. Thermal analysis by differential scanning calorimetry (DSC) found no change in glass transition temperature when comparing pure polystyrene fibers with fibers loaded up to 17 wt % n-Al/PFPE. Thermal gravimetric analysis (TGA) revealed a shift in decomposition temperatures to lower onsets upon increased loadings of n-Al/PFPE blends, consistent with previous studies. Flame propagation studies confirmed that the metallized fibers are pryolants. These metallized fibers are a recent development in metastable intermolecular composites (MICs) and details of their synthesis, characterization, and thermal properties are presented.

KEYWORDS: *nanothermite, pyrolant, energetic material, electrospinning, nanoparticles*

■ INTRODUCTION

Energetic fluorocarbons have been implemented in order to make energetic materials such as propellants and pyrolant flares since the 1950s, the research of which has been recently consolidated in a timely work by Koch.[1] While metal powders are traditionally used as the fuel component in almost all conventional energetic materials, recent efforts have focused on optimizing surface interfaces affording new processing practices for generating novel exothermic materials with more power output and decreased reaction times.[2−8] Metastable intermolecular composites (MICs), a subclass of nanothermites, are made of a mixture of oxidizer and fuel with nanometer-sized particles that allow for energy-dense components to be intimately mixed.[9] In addition to the well-studied, classical metal−fluoropolymer/fuel−oxidizer systems,[10] other recent examples of the fabrication of structural energetic composites include fuel−oxidizer mixtures of aluminum−iron oxide nanocomposite aerosol materials,[6] bio-based thermites,[11] aluminized fluorinated acrylates,[2,12,13] and moldable/post-machinable metallized epoxy-based systems.[14,15]

Of interest to us in this work, the first Al−CuO thermite-based nitrocellulose nanofibers was recently reported by Yan et al. from electrospinning.[16] These 1D nanocomposite energetic textiles led to higher flame propagation rates and increase reaction kinetics due to intimate contact of the thermite formulation decorating the fiber matrix. An additional advantage of electrospinning these MICs is that traditional challenges associated with melt casting or ball milling of nanometallized propellants, for example, pre- or post-burning aggregation, can be mitigated. The technique of electrospinning has been around since the 1930s, but the mechanism behind the spinning was vaguely understood until the 1990s.[17] For the most part, electrospinning is simple and versatile whereby ultrathin polymer composite and ceramic-based fibers can easily be produced. In general, the morphology and diameter of electrospun fibers are dependent on the intrinsic physical properties of the precursor solution (concentration, viscosity, and electrical conductivity) and the operating conditions (strength of the applied electric field, distance between spinneret and substrate, and flow rate of precursor solution).[17]

We have recently reported the fabrication of metallized energetic epoxide-based composites.[15] An energetic blend of nanoaluminum (n-Al) coated with perfluoropolyether (PFPE) (Figure 1) was successfully loaded into a partially cured epoxide and allowed to fully cure. The resulting rigid material did not degrease beyond its glass transition temperature, is indefinitely shelf-stable, and can be post-machined (drilled, milled, or

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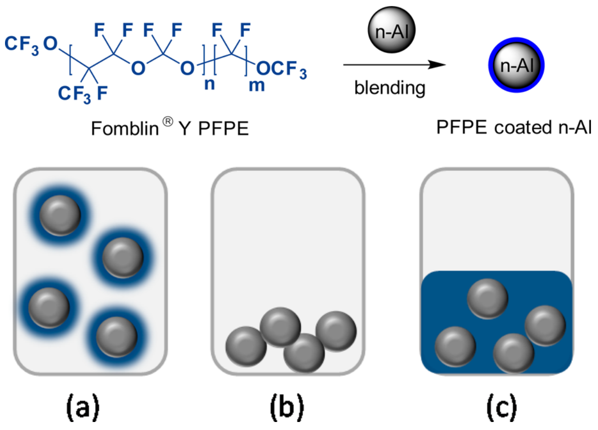

Figure 1. TOP: Blending n-Al with PFPE-produced coated n-Al particles. BOTTOM: (a) When n-Al pre-coated with PFPE is added to a solution of PS/DMF, a viable suspension is formed and metallized fibers can be electrospun. (b) If uncoated n-Al particles (no PFPE) are added to a solution of PS/DMF, the metal particles aggregate and settle out of solution so metallized fibers cannot be electrospun. (c) If PFPE and n-Al are added separately to the PS/DMF solution, separation still occurs and metallized fibers cannot be electrospun.

buffed) into any desirable shape without igniting the component metal, in this case, nanometer-sized aluminum. The metallized epoxide composite exothermically decomposes into the predominating metal-mediated oxidized AlF_3 species as well as competing Al_2O_3 and Al_4C_3 as deflagration products. Based off of these initial findings, we were interested in studying if fibers loaded with the energetic n-Al/PFPE blend could be electrospun in order optimize surface area between the fuel−oxidizer/core−shell particles and the matrix fiber dimensions.

RESULTS AND DISCUSSION

When first approaching the idea of electrospinning fibers and loading them with an energetic blend of n-Al and PFPE, Teflon AF was chosen as the likely precursor polymer to enable electrospinning of the suspension in order to maximize fluorine content of the bulk composite system. Pantoya et al. showed that reaction of micrometer- and nanometer-sized aluminum blended with polytetrafluoroethylene (PTFE or Teflon) is driven to proceed by extraction of fluorine from the PTFE and formation of the thermodynamically stable species AlF_3.[18−20] This reaction is exothermic in nature and the reaction kinetics are well understood and extensively documented in the literature by numerous groups.[1,21−24] Teflon AF, a copolymer of Teflon, seemed like a logical choice for fiber fabrication because it is a solution processable, amorphous thermoplastic. However, in practice, Teflon and Teflon AF are not conducive to electrospinning because of their low dielectric constant values.[25] Initially, our attempts failed to effectively electrospin Teflon AF dissolved in a variety of fluorinated solvents (hexafluorobenzene, Asahiklin AK-225, 3M Fluorinert FC-75). It has been demonstrated that room temperature ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6) can be added to the precursor suspension with a similar partially fluorinated, amorphous polymer in low amounts (>1.5 wt %) to make the suspension more electrospinnable.[26] BMIM-PF_6 was added to a suspension of Teflon AF® yet generation of fibers via electrospinning was still unsuccessful. Teflon AF® has successfully been electrospun by implementing a coaxial electrospinning technique where an electrospinnable polymer is used as a so called guiding material to facilitate spinning.[25,27,28] In one case, poly(vinylidene fluoride) (PVDF) was used as a guiding material, but only 1 wt % Teflon AF® was successfully incorporated into fibers.[25] Instead of attempting coaxial electrospinning, polystyrene (PS) was chosen as the precursor polymer to be electrospun into fibers. Lacking fluorocarbon substitution, PS has a higher dielectric constant and has been employed in the commercial manufacture of electrospun fibers; it was determined PS could serve as a suitable matrix material for this model study.

We also attempted to electrospin fibers loaded with n-Al only (no PFPE), but the metal particles would not remain as a stable suspension in PS/DMF. Similarly, when n-Al and PFPE were added to the PS/DMF solution independently (i.e., were not pre-coated), the constituents of the suspension would also separate. Polystyrene fibers loaded with a uniform distribution of PFPE coated n-Al fibers can only be produced when the pre-coating method is followed to prevent aggregation/agglomeration of the particles. The results are pictorially summarized in Figure 1; suspension separation was observed by eye; however, when photographed, the pictures failed to produce evident contrast. By not pre-coating the n-Al with PFPE, this causes separation of the suspension, clogging the syringe needle, and ultimately resulting in the inability to electrospin uniform metallized fibers. The requirement of pre-coating the n-Al with the PFPE to make the particles miscible with the matrix was also observed when n-Al/PFPE blends were incorporated into epoxide matrices.[15]

Fiber diameters were determined via SEM and representative diameters for a range of fiber loadings are listed in Table 1 and SEM images are shown in Figure 2. As expected, the pure PS fibers appear to have a smooth and regular surface morphology. Pure PS nanometer-sized fibers were consistently achieved; however, upon loading with n-Al/PFPE, microfibers up to 5400 nm diameter were repeatedly achieved with no apparent correlation with wt% loading. A larger variation in diameter was observed for the 17 wt % n-Al/PFPE formulated fibers (1900−7900 nm) whereas electrospinning pure PS consistently produced fibers <100 nm. The relatively wide range of fiber

Table 1. Summary of Physical and Thermal Properties of Fibers

entry	calcd wt% Al/PFPE	exp wt% Al/PFPE	Al bal[c] (%)	avg fiber OD[a] (SEM/nm)	T_d[b] [°C]	T_g[d] [°C]	flame propag velocity (mm/s)
PS standard			1[e]		373	102	
PS fibers			1[e]	80 ± 20	376	103	
n-Al/PFPE PS 1	5	6	7	3900 ± 400	375	100	1.89 ± 0.07
n-Al/PFPE PS 2	10	10	11	1100 ± 400	366	102	1.94 ± 0.30
n-Al/PFPE PS 3	15	17	18	5400 ± 2000	369	103	2.17 ± 0.80

[a] Average of three electrospinning runs. [b] TGA onset of decomposition (5 °C/min) in nitrogen. [c] Residual n-Al balance recorded after 500 °C using TGA (5 °C/min) in nitrogen. [d] DSC (5 °C/min) in nitrogen determined by third heating cycle. [e] Char yield.

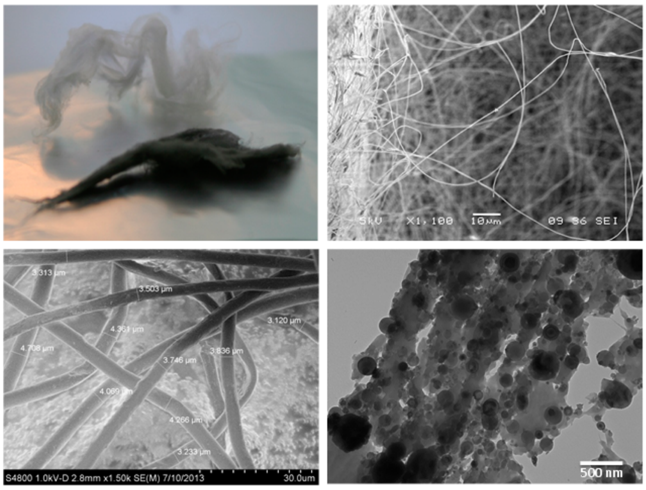

Figure 2. Electrospun control polystyrene fibers (white) and PS fibers loaded with 11 wt % n-Al/PFPE (dark grey) (top left). SEM images of: pure PS fibers (top right), and PS fibers electrospun with 6 wt % n-Al/PFPE (lower left). TEM image of PS fibers electrospun with 17 wt % n-Al/PFPE (lower right).

diameters suggests that while stock solutions appear as homogeneous suspensions, there is inhomogeneity with PFPE treated n-Al, leading to a size distribution of agglomerates. Figure 2 shows a SEM image of PS fibers loaded with 6 wt % n-Al/PFPE that have smooth surfaces and a varying range of diameters (3100−4300 nm). Interestingly, fibers with 10 wt % n-Al/PFPE loadings produced consistently the smallest size distribution (700−1500 nm). TEM analysis showed that the n-Al agglomerates are uniformly distributed on the surface of the fibers. A representative TEM image is shown in Figure 2 with a loading of 17 wt % n-Al/PFPE. The particles appear to be evenly distributed as aggregated of 200−500 nm along the edges of the fiber and are also embedded in the core of the fiber. PS fibers with loadings higher than 17 wt % n-Al/PFPE could not be generated. Varying experimental parameters (viscosity of suspension, working voltage, flow rate, substrate distance, needle gauge) still failed to produce uniform fibers, but rather formed an agglomerated material at higher concentrations. Yan et al. observed similar agglomeration when electrospinning nitrocellulose based fibers and trying to maximize the mass loading of Al/CuO to make energetic thermite textiles.[16] They found that at loadings above 50 wt % nanothermite, the Taylor cone became increasingly unstable, thereby causing severe particle agglomeration.

The thermal stability of the composite fiber system was studied employing TGA and DSC; the resulting measurements for representative fibers are summarized in Table 1. TGA plots of standard PS compared to PS fibers and fibers loaded with n-Al/PFPE blends are shown in Figure 3. Onset of decomposition (T_d) of PS fibers occurs at 376 °C, which agrees with the observed decomposition of standard PS at 373 °C. Low loadings of 6 wt % up to 17 wt % n-Al/PFPE blends did not appear to affect the decomposition temperatures of the fibers. PS and PFPEs are well known to decompose at temperatures >350 °C into volatile aromatic compounds producing char yields <1%.[29−31] For samples loaded with n-Al/PFPE, remaining mass balances are equivalent to the amount of n-Al loaded in the fibers. As seen in Figure 3, at temperatures above the melting transition of Al (T_m of 660 °C), the metal begins to oxidize and the mass balance increases.[32] DSC analysis was performed on all samples and selected plots are also shown in Figure 3. The glass transition temperature (T_g) did not change upon addition of n-Al/PFPE blend (T_g of 102 °C) which is consistent with previous studies on metallized PFPE epoxides. Unlike previous studies, the enthalpy (ΔH) of the thermally-induced Al−F formation could not be determined via DSC. Plots are normalized with respect to T_g, yet a discrete exothermic event could not be distinguished even when comparing pure PS fibers with fibers loaded with the fuel-oxidizer blend. The presence of aluminum in the highest loadings (17 wt % n-Al/PFPE) serves to slightly catalyze degradation of the fibers to an onset of 369 °C; this highest n-Al-loaded composite system still appears to be a suitable for repetitive high temperature service conditions.

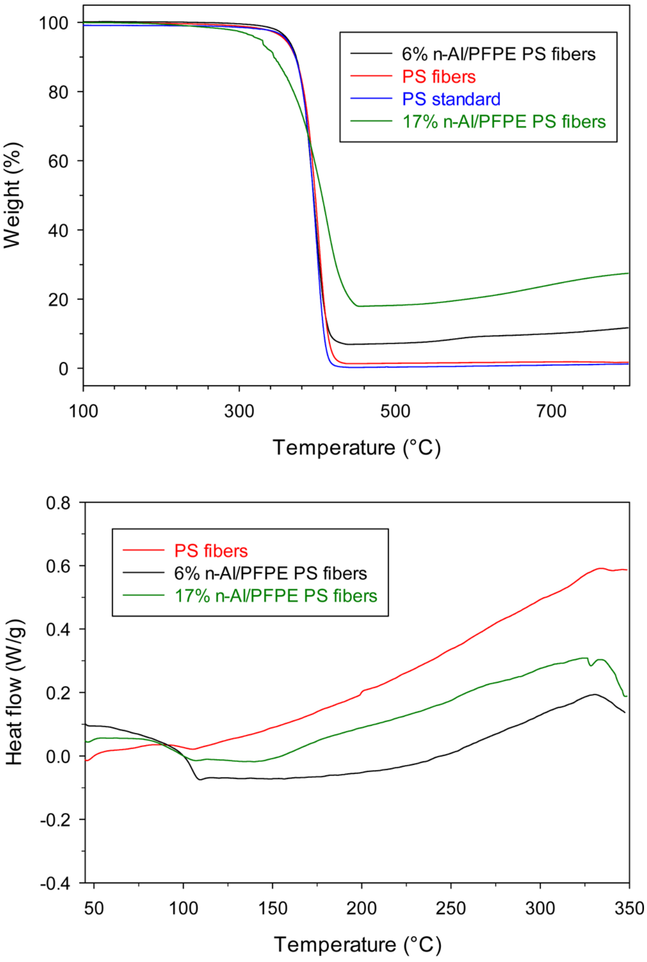

Figure 3. TOP: TGA in N_2 of the standard PS (blue), electrospun PS fibers (red), fibers loaded with 6 wt % n-Al/PFPE blend (black), and fibers loaded with 17 wt % n-Al/PFPE blend (green). BOTTOM: DSC plots of PS fibers (red), fibers loaded with 6 wt % n-Al/PFPE blend (black), and fibers loaded with 17 wt % n-Al/PFPE blend (green). *Y*-axis plotted as exotherm up and plots have been normalized to zero at T_g.

Because thermal analysis did not provide insight into the exothermic nature of the degradation of the samples, flame propagation velocities of composite fibers were determined in addition to thermal analysis. Flame propagation velocities of different samples with varying weight percent loadings of n-Al/PFPE (6−17 wt % n-Al/PFPE) were determined. A schematic of the experimental set-up employed for the determination of the flame propagation velocity of the aluminum-fluoropolymer fiber composite is shown in Figure 4. Rectangular strips of the fibers with 100 mm length and 10 mm width were cut and rolled to obtain a cylindrical cross section along the length of the fiber. These samples were then placed inside a steel combustion chamber (48 × 48 × 48 mm) at room temperature and pressure and ignited using a match. Figure 4 shows sequential snapshots of the progression of the flame front of the fibers burning in the air.

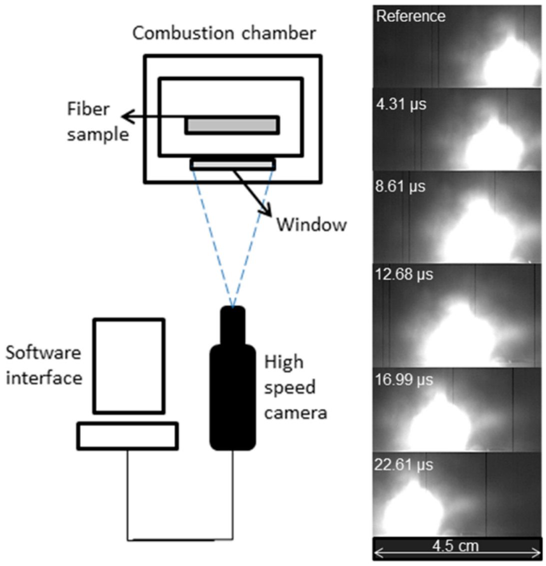

Figure 4. LEFT: Schematic for flame propagation experiments. RIGHT: High speed video camera footage displaying sequential snapshots of 17 wt % n-Al/PFPE fibers burning. Fibers are ignited on the right and the flame front propagates to the left.

Graphical software was used to post-process the recorded photographic data. With an established reference, the software determined flame velocity based on a distance between sequential time frames. Using a "find edge" image filter that identified preset variations in pixel intensity, the flame front location (which was assumed as the region of the flame with the maximum radiance) was identified and marked for velocity measurements. Three tests were conducted on each sample to ensure repeatability of flame propagation velocity measurements and a summary of the results are shown in Table 1. Polystyrene fibers loaded with low amounts of n-Al/PFPE (6 wt %) were found to have a combustion velocity of 1.89 ± 0.30 mm/s and increasing the n-Al/PFPE loading to 17 wt % increased the flame propagation velocity to 2.17 ± 0.80 mm/s. On the basis of the determined flame propagation velocities, the loaded fiber composites are slow burning pyrolants reacting at subsonic speeds <1 m/s and higher n-Al loadings do not appear to influence the rates given the standard deviation in velocities. As a comparison with the only recent report of electrospun pyrolant-based fibers, electrospun nitrocellulose fibers loaded with 50 wt % n-Al/CuO produced reactive textiles that were also found to react at subsonic speeds, albeit about three orders of magnitude faster than n-Al/PFPE fibers at ca. 100 cm/s.[16] This separation implies usefulness for very different applications where propulsion versus localized energy generation as in the case for micro-electro-mechanical systems (MEMS), for example, may be required.

■ EXPERIMENTAL SECTION

Precursor Solution. To prepare the PS solution, 30 wt % bulk PS pellets (commercially available, M_n of 270 000 g/mol by GPC) were dissolved in *N*,*N*-dimethylformamide (DMF, anhydrous, 99.8%, Acros Organics) overnight, at 50 °C in a heater/shaker. Before incorporation into the PS carrier solution, 30 wt % n-Al (US Army Armament Research, Development, and Engineering Center-ARDEC, ca. 80 nm (by TEM), 70% active, ca. 2−5 nm oxide shell) was blended with PFPE (Sigma-Aldrich, Fomblin® Y LVAC 25/6, 3300 g/mol) in a glove box (MBraun Labmaster) under nitrogen. Blends of n-Al/PFPE are weighed directly into a glass screw cap vial and are typically prepared on the 1 g scale. Blends are manually mixed with a spatula for 5 min, capped, and finally removed from the glove box for fiber preparation.

Previous experimental studies employing PFPEs to coat different weight percent n-Al revealed the optimized stoichiometric ratio producing the largest enthalpy of reaction (ΔH) to be 30 wt % n-Al fuel to 70 wt % PFPE oxidizer.[15] Thus, a blend of 30 wt % n-Al in PFPE is implemented in the current study to prepare fibers. The desired amount of n-Al/PFPE blend is added to the PS/DMF solution. The suspension is manually mixed with a spatula for 5 min and then ultrasonicated for 5 mins. The suspension is immediately electrospun within 10 min. If the suspension is not immediately used for fiber preparation, the solids irreversibly precipitate out of the DMF solution as a solid block within 12 h. Weight percent loadings of n-Al were initially calculated and weighed in order to prepare the precursor solution. After fibers were electrospun, the sample was measured to determine the residual Al content at 500 °C using TGA (5 °C/min) in nitrogen which was used to back-calculate the n-Al/PFPE loading. These measurements were performed because although the precursor suspensions are relatively stable for short periods of time (<0.5 h), some settling out of the Al does occur altering the transferred mass balance during electro-spinning.

Fiber Spinning. An in-house electrospinning setup in a fume hood is used to electrospin the metallized suspension equipped with syringe pump (KD Scientific model 100 syringe pump), target plate, and accompanying voltage supply (EL Glassman High Voltage source). In order to reduce the chance of spark ignition while electrospinning, a low working voltage of 12−15 kV, is applied to a stainless steel needle (17−27 gauge) thereby charging the n-Al/PFPE loaded PS/DMF suspension. The syringe pump is set at a flow rate of 0.5−1.25 mL/h and non-woven fiber mats are collected 76−100 mm from the needle tip onto a square target plate (75 mm × 75 mm) covered in aluminum foil. Control PS fibers without any n-Al or PFPE were also electrospun using the conditions discussed above in order to validate the reproducibility of the electrospinning apparatus. When loaded with a blend of PFPE coated n-Al particles, the fibers become dark grey and appear denser than the control PS fibers without any additives (Figure 2).

Thermal Analysis and Microscopy Characterization. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) was performed on a TA Q500 and TA Q20, respectively. Measurements were performed under N_2 atmosphere at a rate of 5 °C/min. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) was performed on a Hitachi S-4800 (Clemson University Electron Microscopy Facility) or a JEOL 6460 LV and Hitachi H-7600 (Clemson University Electron Microscopy Facility), respectively.

Flame Propagation Analysis. A Phantom v7 (Vision Research, Inc., Wayne, NJ) with a Nikon AF Nikkor 52 mm 1:2.8 lens was used to record ignition and flame propagation of the mixtures. The camera captured images of the burning fiber composite, perpendicular to the direction of flame propagation, with a resolution of 256 × 128 pixels.

■ CONCLUSION

In summary, we were able to successfully electrospin polystyrene fibers loaded with an energetic formulation of n-Al particles pre-coated with PFPE. Thermal analysis revealed that increased loadings of n-Al/PFPE results in a decrease in temperatures of decomposition consistent with previous work on epoxy-based metallized bulk composites. Flame propagation studies confirm similar combustion rates with increased loadings of the energetic blend into the fibers. Electrospinning of energetic fibers is a novel way to prepare pyrolant mats. Selecting other polymer systems to electrospin with n-Al/PFPE blends in order to explore other morphologies may increase the flame propagation velocities of fibers, and would be the next logical concentration for on-going work.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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