

# Thermal Data of Perfluorinated Carboxylic Acid Functionalized Aluminum Nanoparticles

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**Abstract:** Improving the performance of composite energetic materials comprised of a solid metal fuel and a source of oxidizer (known as thermites) has long been pursued as thermites for pyrolant flares and rocket propellants. The performance of thermites, involving aluminum as the fuel, can be dramatically improved by utilizing nanometer-sized aluminum particles (nAl) leading to vastly higher reaction velocities, owing to the high surface area of nAl. Despite the benefits of the increased surface area, there are still several problems inherent to nanoscale reactants including particle aggregation, and higher viscosity composited materials. The higher viscosity of nAl composites is cumbersome for processing with inert polymer binder formulations, especially at the high mass loadings of metal fuel necessary for industry standards. In order to improve the viscosity of high mass loaded nAl energetics, the surface of the nAl was passivated with covalently bound monolayers of perfluorinated carboxylic acids (PFCAs) utilizing a novel fluorinated solvent washing technique. This work also details the quantitative binding of these monolayers using infrared spectroscopy, in addition to the energetic output from calorimetric and thermogravimetric analysis.

**Dataset:** Supplementary file of thermal analysis

**Dataset License:** CC-BY

**Keywords:** energetics; pyrolants; fluorine; nanoaluminum; carboxylic acids; nanoparticles; metal fuels; oxidizers; calorimetry; monolayer



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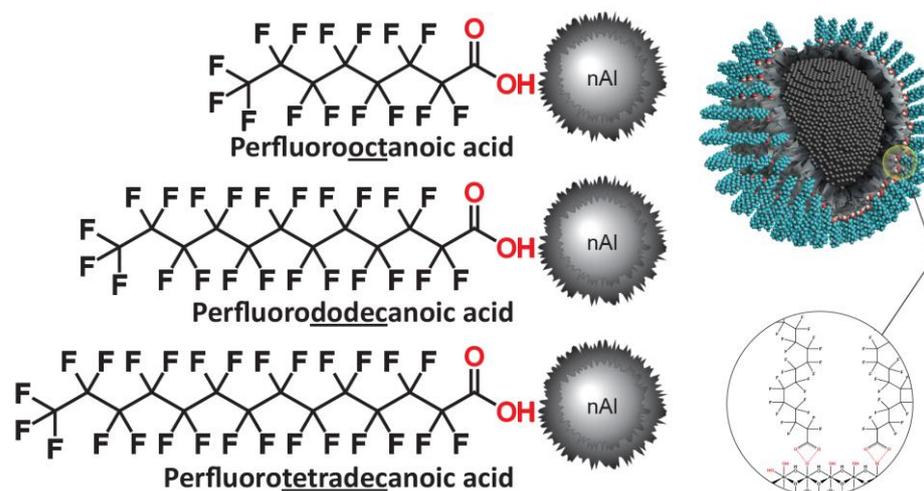
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## 1. Summary

A comprehensive set of spectroscopy and thermal data of nanometer-sized aluminum (nAl, the metal fuel) functionalized with a series of perfluorinated carboxylic acids (PFCA, the oxidizer) core-shell thermite particles are provided in this article. Specifically, the PFCA oxidizer series includes perfluorooctanoic acid (PFOA), perfluorododecanoic acid (PFDA), and perfluorotetradecanoic acid (PFTA) that were solvent blended and washed repeatedly onto 100 nm nAl and confirmed as covalently bound monolayers by attenuated total reflectance infrared spectroscopy (ATR-IR) as shown in Figure 1. Differential scanning calorimetry data provided the metal/fuel (core/shell) particles with melt transitions and exothermic enthalpies of the oxidation of the nAl fuel. In addition, thermogravimetric analysis data provided onset of degradation and char yields that provided a quantitative assessment of the PFCA monolayer.

The data provided in this work are unpublished and were part of a larger embodiment of our work on “Optimizing the Interfaces of Energetic Textiles with Perfluorinated Oligomer-Coated Aluminum Nanoparticles: Implications for Metastable Intermolecular Composites” [1]. The relevance for providing these thermal data is to demonstrate to the broader community of experimental research in fluorine-containing oxidizers for metal fuels, an area that has been recently and extensively reviewed [2], a novel fluorinated solvent

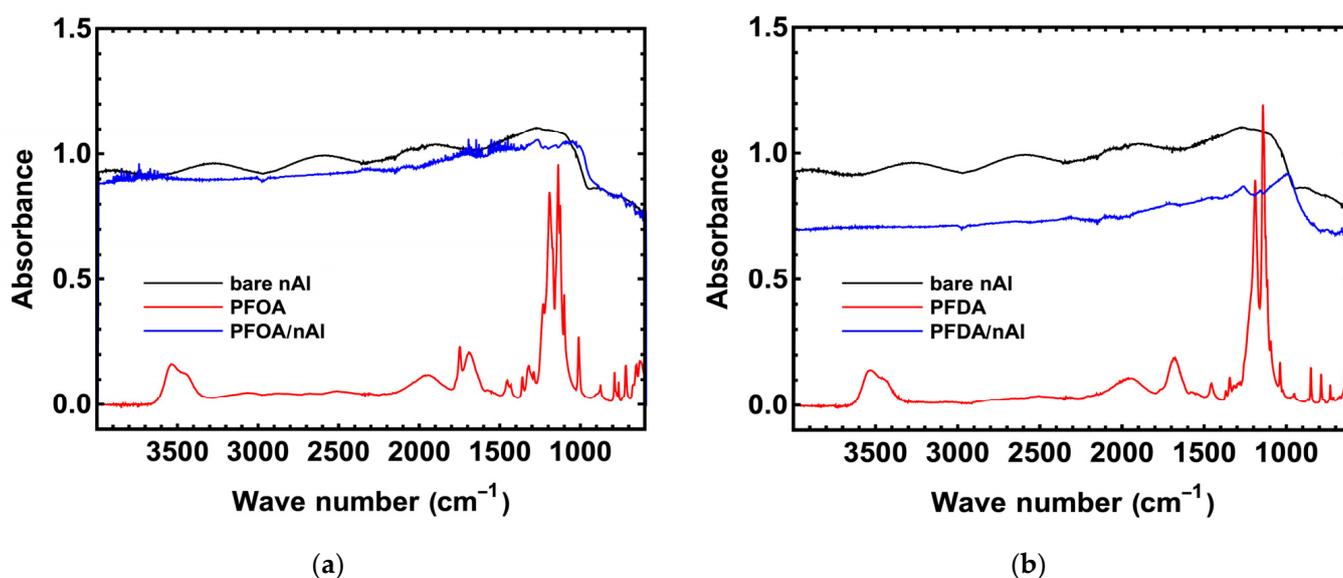
washing processing technique for improved intermolecular PFCA monolayers onto metal fuels. This information, herein, may also be helpful to researchers involved with challenges in formulating bulk polymer composites possessing organo-fluorine components with metal particulates by conventional solvent or melt processing, in addition to advanced manufacturing practices.



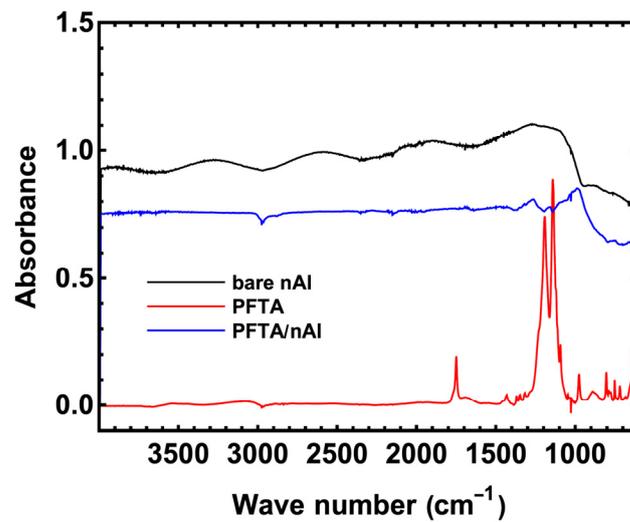
**Figure 1.** Chemical structure depiction of varying fluoroalkyl chain lengths of PFCAs, PFOA, PFDA, and PFTA covalently bound monolayers onto nAl particles' surfaces and a visual depiction of bulk core/shell bound PFCA/nAl particle.

## 2. Data Description

The three sections for data description for analysis of PFCA/nAl particle formulations include: (1) ATR-IR data demonstrating monolayer attachment of PFCA onto nAl (Figure 2), (2) DSC data of solvent processing and efficacy of thermal exotherms at multiple solvent washings (Figure 3), and (3) TGA data of selected PFCA/nAl particles' formulations and their onset of degradation and residual char yields (Figure 4). Table 1 provides a summary of selected data of ATR-IR, DSC, and TGA data.

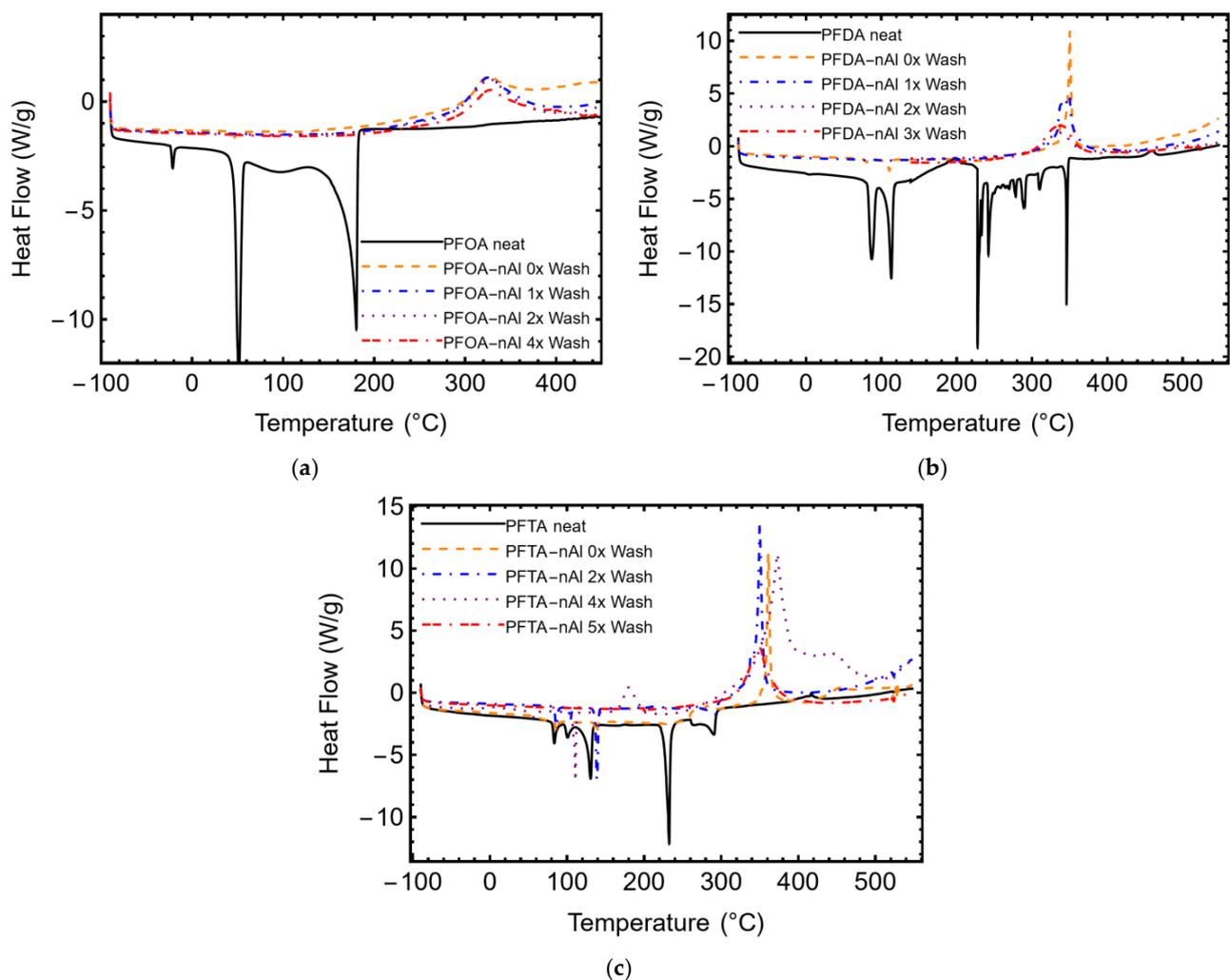


**Figure 2.** *Cont.*



(c)

**Figure 2.** ATR-IR spectra of bare nAl, PFCA neat; and washed PFCA/nAl core/shell particle: (a) PFCA is PFOA; (b) PFCA is PFDA.; (c) PFCA is PFTA.

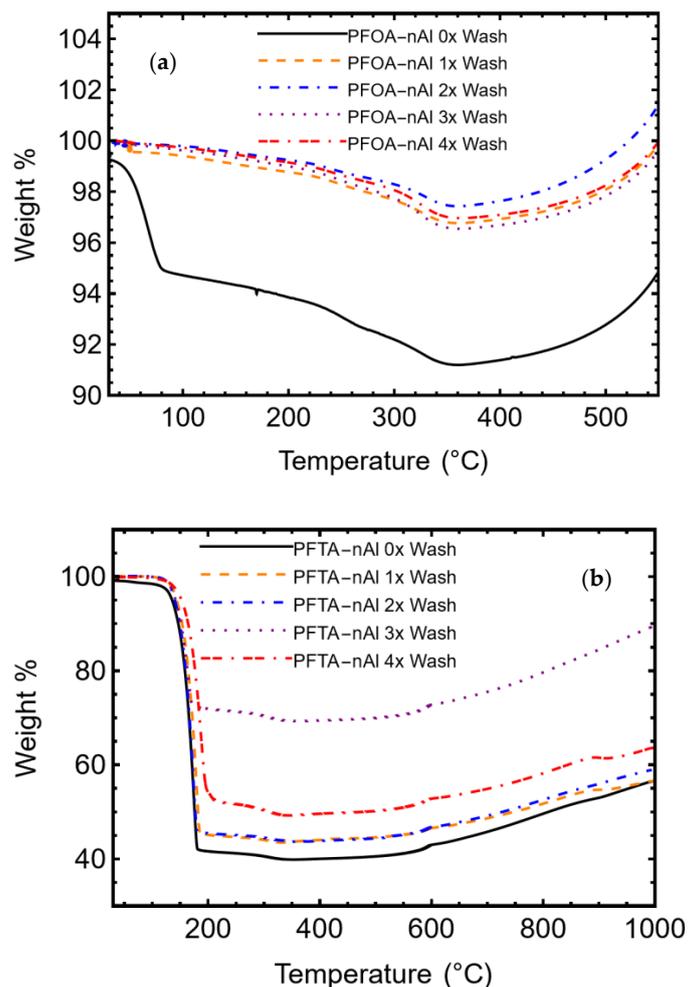


(a)

(b)

(c)

**Figure 3.** DSC thermograms of PFCA neat and stacked overlays of PFCA/nAl core/shell particle after multiple washings: (a) PFCA is PFOA; (b) PFCA is PFDA; (c) PFCA is PFTA.



**Figure 4.** TGA thermograms of PFCA neat and stacked overlays of PFCA/nAl core/shell particle after multiple washings: (a) PFCA is PFOA; (b) PFCA is PFTA.

**Table 1.** Selected ATR-IR, DSC, and TGA data of PFCA coated nAl particles.

Entry	Wash	$\bar{\nu}$ (cm <sup>-1</sup> )	$T_m$ (°C)	$\Delta H_{exo}$ (J/g)	$T_d$ (°C)	Char Yield (%)
nAl (bare)	–	–	–	–	–	–
PFOA	–	1140, 1200	–24, 40	–	147.	–
PFDA	–	1150, 1200	82, 10	–	227	–
PFTA	–	1150, 1200	80, 97, 121	–	221	–
PFOA/nAl	0×	–	41	121	302	94
PFOA/nAl	1×	–	–	189	291	97
PFOA/nAl	2×	–	–	190	289	97
PFOA/nAl	3×	–	–	187	287	96
PFOA/nAl	4×	1180, 1230	–	185	293	96
PFDA/nAl	0×	–	80, 108	189	347	–
PFDA/nAl	1×	–	80, 107	219	331	–
PFDA/nAl	2×	–	–	196	306	–
PFDA/nAl	3×	1170, 1280	–	190	304	–
PFTA/nAl	0×	–	83, 133	276	357	40
PFTA/nAl	1×	–	82, 102, 133	236	346	43
PFTA/nAl	2×	–	82, 102, 133	222	346	43
PFTA/nAl	4×	–	65, 106	228	358	49
PFTA/nAl	5×	1180, 1270	–	227	322	–

### 2.1. ATR-IR Data

The ATR-IR data of PFOA, PFDA, and PFTA coated nAl particles are shown in Figure 2, and compared with bare nAl particles and the respective neat PFCAs. For the PFCA-coated particles, the presence of a C=O stretch—characteristic of a carboxylic acid moiety coordinated to alumina in the ATR-IR spectra of the solvent washed particles (up to three times)—confirms the attachment of the carboxylate ( $-\text{COO}^-$ ) end groups of the PFPE DC to the nAl surface via bridging mode, as identified by COO antisymmetric, and COO symmetric stretches at  $1650$  and  $1480\text{ cm}^{-1}$ , respectively [1].

### 2.2. DSC Data

Figure 3 shows DSC plots for each PFCA series (neat) and PFCA coated nAl particles with multiple washings with a fluorinated solvent, specifically a blend of Fluorinert FC-75 and 2H,3H-perfluoropentane. The thermograms show heating, initially from  $-100\text{ }^\circ\text{C}$  to  $450\text{ }^\circ\text{C}$  at a rate of  $5\text{ }^\circ\text{C}/\text{min}$ , and heat flow ( $W/g$ ) which is recorded with exotherms as positive values. For neat PFCAs, multiple endothermic melting transitions ( $T_m$ ) are shown. The exotherms of the PFCA coated nAl particles range consistently with onset at  $250\text{ }^\circ\text{C}$  to  $400\text{ }^\circ\text{C}$  with exothermic maxima ( $T_{max}$ ) at  $350\text{ }^\circ\text{C}$ . The  $T_{max}$  intensity attenuates after multiple washings, specified in Figure 3, until the threshold of washings is reached.

### 2.3. TGA Data

Enhanced TGA plots for each PFCA series (neat) and PFCA coated nAl particles with multiple washings were formulated (Figure 4). The thermograms provided in the Supporting Information were heated initially from  $20\text{ }^\circ\text{C}$  to  $900\text{ }^\circ\text{C}$  at a rate of  $0.5\text{ }^\circ\text{C}/\text{min}$  in nitrogen, and recorded with decreasing weight percentage (wt%). For unwashed PFCA/nAl samples ( $0 \times$  wash), onset of initial weight loss was significant and consistent with sublimation of excess PFCA which was accumulated at the TGA flow gas exhaust as a white semi-crystalline solid. The onset of degradation ( $T_d$ ), after subsequent washing of the PFCA coated nAl particles, increased in wt% retaining the PFCA coated monolayer. Charring of the PFCA coated nAl particles at different wash cycles is observed after  $200\text{ }^\circ\text{C}$  with the remaining mass balance of residual aluminum. Oxidation of Al to aluminum oxide ( $\text{Al}_2\text{O}_3$ ) is observed, producing off-white solids after heating beyond  $350\text{ }^\circ\text{C}$  as indicated in the TGA, with mass update due to adventitious air in the nitrogen carrier gas. Data for formulations of PFDA coated nAl particles were left out given the limited stock of nAl available at the time of this study.

## 3. Methods

### 3.1. Materials

Aluminum nanometer-sized powder (denoted nAl) with an average particle size of  $100\text{ nm}$  and a specific surface area of  $25\text{ m}^2/\text{g}$  was obtained from U.S. Research Nanomaterials and stored under nitrogen atmosphere. The powder had 75% active Al content by mass, as designated by the manufacturer analysis specification sheet. Perfluorooctanoic acid (PFOA), perfluorododecanoic acid (PFDA), and perfluorotetradecanoic acid (PFTA), Fluorinert FC-75, and 2H,3H-perfluoropentane were obtained from SynQuest Laboratories and used as received.

### 3.2. Instrumentation

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were collected using a Thermo Nicolet FTIR spectrometer iS10. Differential scanning calorimetry (DSC) was performed on a TA Auto Q20 Instrument in nitrogen. Samples (ca.  $5\text{ mg}$ ) were sealed in an aluminum hermetic pan with an empty sealed hermetic pan serving as the reference. Thermal transitions were reported on the third heating cycle and values recorded at the mid-point, unless otherwise specified. Samples were heated/cooled at a rate of  $5\text{ }^\circ\text{C}/\text{min}$ . Thermal gravimetric analysis (TGA) was performed on a TA Q500 instrument at a scan rate of  $0.5\text{ }^\circ\text{C}/\text{min}$  in nitrogen. Samples ( $5\text{--}10\text{ mg}$ ) were measured with

a platinum crucible and heated from room temperature to 900 °C. TA Universal Analysis 2000 graphical software was used to determine the thermal properties.

### 3.3. Oxidizer/Fuel Core-Shell Particle Synthesis

nAl (1.0 g), PFCA (0.50 g), Fluorinert FC-75 (30 mL), and 2H,3H-perfluoropentane (60 mL) were added sequentially to a flame-dried, 3-neck round bottom flask, and sealed with rubber septa under nitrogen. The mixture was then sonicated for 30 min to further homogenize the particles in the solution. The suspension was then refluxed (~80 °C) under N<sub>2</sub> flow for 24 h. After refluxing, suspended particles were washed with a fresh mixture of 2H-3H-perfluoropentane. The washing was accomplished by repeatedly isolating the particles with centrifugation, and then through sonication-aided dispersal in fresh solvent. The PFCA/nAl formulations were found to be resistant to oxidation when stored for long periods (>10 weeks) in air, as confirmed by comparison of DSC analysis of newly created and stored batches.

*POTENTIAL HAZARD NOTE: In our studies, the preparation of PFCA/nAl blends showed indefinite shelf-stability in open air and during physical handling of the materials. These materials were/should be prepared on a small-scale with less than 1 g nAl content. However, we stress caution in handling these materials by using the proper personal protection equipment (gloves, safety glasses, and a flame retardant garment) and in a glove box or under a controlled inert air-handling environment and preferably in a ventilation fume hood. Avoid exposing materials to an open flame, static discharge, direct heating, or other energy point sources (unless under controlled conditions and by an individual experienced in the art) as these formulations are extremely flammable and potentially combustible.*

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/data8010005/s1>, DSC and TGA data related to Figures 3 and 4.

**Author Contributions:** Conceptualization, N.J.W. and S.T.I.; methodology, N.J.W., B.M. and E.G.; writing—original draft preparation, N.J.W. and S.T.I.; writing—review and editing, N.J.W. and S.T.I.; project administration, S.T.I.; funding acquisition, S.T.I. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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1. Weeks, N.J.; Gazmin, E.; Iacono, S.T. Optimizing the interfaces of energetic textiles with perfluorinated oligomer-coated aluminum nanoparticles: Implications for metastable intermolecular composites. *ACS Appl. Nano Mater.* **2021**, *4*, 6002–6011. [[CrossRef](#)]
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