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SYNTHESIS AND REACTIVITY OF ALUMINIZED FLUORINATED ACRYLIC (AlFA) NANOCOMPOSITES (POSTPRINT)

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14. ABSTRACT

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Synthesis and reactivity of aluminized fluorinated acrylic (AlFA) nanocomposites

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1. Introduction

Aluminum powders are a critical ingredient in the formulation of many energetic materials, including some explosives and pro pellants, added to increase energy densities within these systems as well as enhance their flame temperatures and pressures [1]. Micron scale aluminum (micron Al) powders are used in nearly all conventional metalized energetic materials, however, the ad vent of technologies to produce high quality nano scale aluminum powders (nano Al) has led to the exploration of nano Al as a replacement for micron Al in certain formulations [2,3]. The inter est in nano Al as a replacement for larger micron Al powders stems from the dramatic increase in specific surface area (SSA) that is obtained as a result of the small particle size of the nano pow ders. The large SSA, typically 25 40 m^2/g, yields an increase in the reactive performance of these materials due to the close prox imity of the fuel (nano Al) and oxidizing components of these sys tems, as the kinetics for these reactions are generally limited by mass transport (diffusion) between the reacting species [1,4]. For example, substitution of nano Al for micron Al in a thermite mix ture, e.g., aluminum powder mixed with a metastable metal oxide (Fe_2O_3, CuO, Bi_2O_3, WO_3, etc.), can lead to an increase in the rate of reaction by up to three orders of magnitude [5,6].

Fluorinated materials, specifically fluorinated polymers such as poly(tetrafluoroethylene) (PTFE) and its co polymers, fluorinated elastomers, and molecular fluorocarbons have recently received significant attention as suitable oxidizer materials for nano Al [7 9]. The stoichiometric reaction of Al with a pure fluorocarbon (e.g., PTFE; $\Delta H_F =$ 809.60 kJ/mol) [10] yields elemental carbon and aluminum trifluoride as shown in the following equation:

$$2Al + 3(-CF_2-)_n \rightarrow 3C + 2AlF_3, \quad \Delta H^0 \quad 591.98\ kJ \qquad (1)$$

Formation of AlF_3 ($\Delta H_F(AlF_3) =$ 1510.39 kJ/mol) yields 56.10 kJ/g of Al which is nearly twice the energy liberated by reacting Al with oxygen to yield Al_2O_3 ($\Delta H_F(Al_2O_3) =$ 1675.72 kJ/mol), which re sults in 30.98 kJ/g of Al [11]. Additionally, AlF_3 begins to sublime at 1276 °C well below the combustion temperature of nano Al [11]. As AlF_3 volatilizes it should leave behind a fresh aluminum surface which can enhance the kinetics of the reaction as there is less build up of product on the particle surface to inhibit diffusion between the reactants. This is contrary to aluminum oxidation where the combustion temperature is limited to an extent by the vaporization temperature of the oxide ($T_{vap} =$ *ca.* 3000 3700 °C) as more oxide is formed the reaction rate can actually begin to slow down due to the presence of the dense molten alumina at the sur face of the particle, since the boiling temperature of aluminum is less than the vaporization temperature of the oxide the aluminum

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fuel must diffuse through the oxide to react with oxygen in the va por phase [11,12]. The potential increase in liberated energy and energy release rate makes fluorinated materials viable alternatives to conventional metal oxide powders in several applications.

Reactive mixtures where the fuel and oxidizer components are both powders (e.g., Al and Fe_2O_3) are typically consolidated by powder compaction. This often results in a material that is brittle due to an absence of chemical bonding and/or strong physical interaction between the individual particles. The mechanical prop erties of pressed powder composites can be improved by the addi tion of a binder material, however, these materials are often inert and subtract from the performance of the material [13]. Addition ally, due to the high SSA of the nano powders, a significant amount of binder is required to provide complete coverage of the powders. The addition of fluorinated polymers, or reactive polymers in gen eral, as either an oxidizer or reactive binder has the potential to introduce useful mechanical properties into these reactive powder mixtures. Reactive mixtures of nano Al with PTFE or PTFE/Viton represents current state of the art for reactive nano Al/fluoropoly mer systems [7,8,14]. In most literature reports these composites are prepared by sonochemical mixing of nano Al with PTFE or PTFE/Viton powders in a solvent to evenly distribute and increase contact between the components. Consolidation of the mixtures is achieved by evaporation of the solvent and compression of the mixed powders into pellet form [7,15]. Fluoropolymers are soft in comparison to nano Al and the composites can often be pressed to near uniform density without undergoing any elevated temper ature processing or sintering. However, the consolidated pressed powder composites have minimal chemical and/or physical inter action between the individual component particles (poly mer + metal and polymer + polymer), and thereby fail to achieve adequate mechanical properties. To obtain better bonding between the individual components, additional processing steps such as sin tering or extrusion can be performed, however, sintering of PTFE is typically performed at temperatures above 300 400 °C which is near the temperature required to initiate pre ignition reactions; i.e. reactions with the amorphous aluminum oxide shell on nano Al [9]. Processing of PTFE by extrusion is also not possible without addition of other chemicals and/or solvents or modification of the polymer backbone to yield a co polymer [16].

Herein we report a new approach towards the preparation of nano Al/fluoropolymer composites, comprised of functionalized nano Al chemically integrated into a fluorinated methacrylic poly mer through an *in situ* polymerization process. These aluminized fluorinated acrylic nanocomposites, which we have termed AlFA composites, show good bonding at the polymer and particle inter face and exhibit thermoplastic behavior allowing them to be pro cessed using conventional polymer processing techniques such as melt extrusion. A detailed description of the synthetic approach and characterization of their physical properties and reactive behavior is discussed.

2. Experimental

2.1. Chemicals

Aluminum nanoparticles (80 nm, 80% active Al content) were obtained from Novacentrix, Inc. and were stored under argon in a glove box ($O_2 \leqslant 1$ ppm; dew point = 80 °C) prior to use. Cyclohex anone, phosphoric acid 2 hydroxyethyl methacrylate ester (PAM) and 2,2′ azobis(2 methylpropionitrile) (AIBN) were acquired from Aldrich and used as received unless otherwise noted. 1H,1H,2H,2H perfluorodecyl methacrylate (PFDMA) was obtained from Synquest Laboratories and purified by vacuum distillation and stored under nitrogen in a refrigerator (4 °C) prior to use. Cyclohexanone was dried over CaH_2 and distilled prior to use in the polymerizations. AIBN was recrystallized from acetone prior to use.

2.2. Synthesis of PAM co nano Al

The procedure used for the surface functionalization of nano Al with PAM prior to composite formation was adapted from previous literature [17]. A typical reaction for the functionalization of nano Al with PAM to yield PAM *co* nano Al was performed as follows. A 1000 mL four necked reaction vessel, fitted with an overhead stirrer, two rubber septa, and a glass stopper was charged with nano Al powder (30.0 g, 1.11 mol) and hydroquinone (0.050 g, 0.45 mmol), which was added as a radical scavenger to prevent polymerization during the reaction. PAM (2.97 g, 12.5 mmol) [18] was dissolved into 250 mL of cyclohexanone and transferred to the reaction vessel and stirred (235 rpm). A nitrogen atmosphere was established and maintained in the reac tion vessel throughout the course of reaction. The vessel was then submerged into an external oil bath at 60 °C and reaction was allowed to progress for 4 h. The functionalized particles were iso lated by vacuum filtration over a 0.2 μm PTFE membrane (Cole Parmer) and washed with cyclohexanone and acetone to remove physisorbed PAM. The filtered product was then dried in a vacuum desiccator to remove residual solvent prior to analysis. Organic content of the PAM *co* nano Al was determined to be *ca.* 4% by weight.

2.3. Synthesis of aluminized fluorinated acrylic (AlFA) composites

AlFA *X* (where *X* denotes the particle content in terms of parti cle wt.%) composites were prepared by *in situ* polymerization of PFDMA with varying concentrations of PAM *co* nano Al as indi cated in Table 1. A typical polymerization for the preparation of AlFA 30 was carried out using the following procedure. A 1000 mL four necked reaction vessel fitted with an overhead stirrer and three rubber septa was charged with PAM *co* nano Al (15.0 g) and AIBN (0.350 g, 2.13 mmol). The vessel was then sealed and placed under a nitrogen atmosphere. PFDMA (35.0 g, 65.8 mmol) was added via syringe to the reaction vessel followed by dry cyclohexanone (75 mL) which was transferred via canula to serve as the solvent. The reaction mixture was subjected to three purge freeze pump thaw cycles to remove dissolved oxygen. Upon completion the mixture was stirred at 235 rpm and the reac tion vessel was submerged into an external oil bath held at 75 °C for a minimum of 4 h. In most cases polymerization was completed prior to 4 h and could be observed by an increase in viscosity and precipitation of the composite from the solvent, however, the reac tion was still held at temperature for 4 h to ensure the complete polymerization. After 4 h the heat was removed and the reaction was allowed to cool to room temperature. The composite was re moved from the reaction vessel, transferred to a filtration appara tus fitted with a 0.2 μm PTFE membrane and washed with acetone to remove cyclohexanone and any unreacted monomer. The fil tered product was then dried in a vacuum desiccator to remove

Table 1
Reaction conditions for the synthesis of AlFA composites.

Composite	PAM-*co*-nAl (g)	PFDMA (g)	AIBN (g)	Cyclohexanone (mL)
AlFA-0	–	50.0	0.50	75
AlFA-10	5.0	45.0	0.45	75
AlFA-30	15.0	35.0	0.35	75
AlFA-50	25.0	25.0	0.25	75
AlFA-60	30.0	20.0	0.20	75
AlFA-70	35.0	15.0	0.15	75

residual solvent. Reaction yields between 90% and 95% were ob served for each composite.

To ensure uniform distribution of the nano Al throughout the material, the composite was compounded for 3 min in a DACA Instruments benchtop twin screw extruder at 150 °C. The com pounded material was then extruded through a circular die into a cylindrical clam shell mold and allowed to cool to room temper ature. The final product was a gray, waxy solid with increasing metallic luster as particle content increased; the AlFA 0 composite, which does not contain any nano Al, was a white waxy solid.

2.4. Characterization

Thermogravimetric analysis (TGA) was performed on a TA Instruments SDT Q600 dual TGA/DTA. Samples (5 20 mg) were placed into a tared alumina crucible with an empty alumina cruci ble serving as the reference. All data was collected in dynamic mode under flowing argon (100 mL/min) from room temperature up to 800 °C at a rate of 5 °C/min.

Differential Scanning Calorimetry (DSC) was performed on a TA Instruments Q1000 DSC. Samples (3 10 mg) were sealed in an alu minum pan with an empty aluminum pan serving as the reference. Each sample was subjected to a heat cool heat cycle to remove any stored thermal history in the material. After equilibrating at 90 °C samples were heated at 5 °C/min to a final temperature of 150 °C. Following the first heating cycle the samples were cooled from 150 °C to 90 °C at a rate of 5 °C/min and then subjected to a second heat ramp covering the same temperature range at 2 °C/min. All reported data was collected during the final heating cycle.

Transmission electron microscopy (TEM) images were acquired on a Phillips CM200 microscope with LaB_6 emission source at an operating voltage of 200 keV. Samples were prepared by embed ding small slivers of the composites into flat molds filled with EMbed 812 resin and polymerized overnight in a 60 °C oven. The blocks were then ultramicrotomed with a PowerTome XL ultrami crotome by Boeckler Instruments and a 35° Diatome diamond knife. Sections were cut at a thickness of 75 nm and a speed of 1 mm/s. Ribbons of the sections were floated onto the water trough of the diamond knife and picked up and placed onto 3 mm 400 mesh hexagonal Cu grids and allowed to air dry. Once dry, the sec tions were ready to be imaged in the TEM.

Pellet combustion experiments were performed by placing an 8 mm long × 4 mm diameter pellet of the respective composite onto a stainless steel wire mesh located in a vented fragmentation chamber under an air atmosphere. The pellets were initiated by a butane flame from directly below. A NAC Image Technology Mem recam® GX8 digital high speed video camera, collecting full frame, full color images at 3000 frames per second, was used to record vi deo of the pellet combustion experiments. Images from the high speed video were subsequently analyzed using image processing software (IDL 3.1) in order to calculate intensity of reaction (light output) as a function of time.

X ray powder diffraction (XRD) spectra were acquired on a Rig aku DMAX B RU200 spectrometer using Cu Kα radiation. Identifica tion of the observed patterns was accomplished by comparison with the ICDDS crystallographic database.

Quasi static compression testing of 8 mm long × 4 mm diame ter right circular cylinders was carried out using an MTS 820 servo hydraulic test frame, incorporating a self aligning compres sion subpress (Wyoming Test Fixtures, model B 11) with precision ground steel upper and lower platens. Testing was per formed according to ASTM D695 10 under displacement control at a nominal strain rate of 10^{-3} s^{-1}. A digital video camera and associated image correlation software (Vic Gage 2.0: Correlated Solutions, Inc.) was used to record continuous strain data from multiple, redundant *virtual* strain gages during the testing. Simul taneous load data was obtained using a calibrated 10 kN load cell mounted on the load frame. Teflon® tape was used to lower the friction between the specimen end faces and both upper and lower loading platens, to minimize barreling. A minimum of two repeat specimens were tested for each AlFA composition.

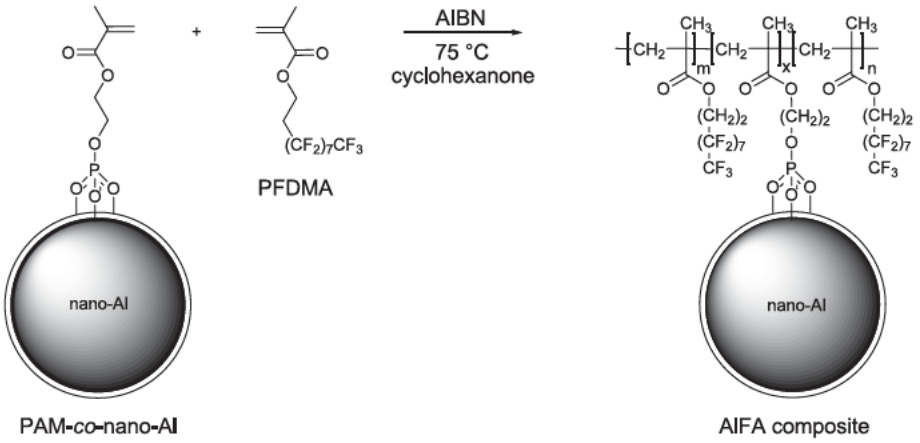
3. Results and discussion

To date, PTFE has been the most prominently reported fluori nated precursor used in nano Al/polymer composite reactive sys tems. This is due in part to its fully fluorinated carbon backbone resulting in a fluorine density of 75% by weight, higher than any other fluorinated polymer system. Additionally, PTFE is available in both micron and nano scale powders that are amenable to mix ing with nano Al. The main limitation of PTFE is its processability. Suspension or dispersion polymerizations are commonly used to prepare high quality PTFE [16], however these approaches require the use of both an aqueous layer and elevated temperatures, which limits the possibly of introducing nano Al to prepare nano Al/PTFE composites *in situ* since nano Al reacts with water, especially at elevated temperatures. In the present work, therefore, a solution polymerization approach was selected which would not compro mise the reactivity of nano Al. Secondly, a monomer system was required that could be polymerized *in situ* with the functionalized nano Al particles and one that would yield a more processable polymer than PTFE. PFDMA was chosen since it has a highly fluori nated alkyl tail, analogous to a PTFE oligomer and contains *ca.* 60% fluorine by weight. PFDMA also contains a readily polymerizable methacrylic head that is amenable to free radical polymerization and is similar in structure to the PAM used to functionalize the nano Al. Furthermore, PFDMA was commercially available at a moderate cost and is compatible with many solvents making it desirable for solution polymerization.

The presence of a solvent was necessary to overcome the com mon viscosity and wetting issues related to the high SSA of the nano Al particles; cyclohexanone was selected to provide dissolu tion of the heavily fluorinated monomer, PFDMA, thereby allowing it to react with the functionalized particles during polymerization. The acting hypothesis was that the monomer coating present on the nano Al surface would co polymerize during propagation of the growing poly(PFDMA) chains thereby providing a direct chem ical linkage between the particles and the polymer matrix. The general reaction scheme is presented in Scheme 1.

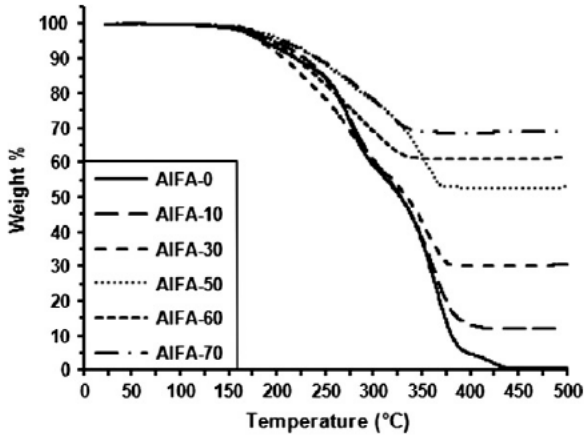
The thermoplastic behavior of the poly(PFDMA) matrix allowed for successful compounding of all AlFA composites with the excep tion of the AlFA 70 composite. The particle content was sufficient in the AlFA 70 powder to seize the screws in the compounder. A picture of a typical processed and machined AlFA composite is dis played in Fig. 1. It is worth noting that the physical appearance of the composites increases in metallic luster as the particle content is increased.

TGA analysis was performed to confirm the particle loading of the composite materials after compounding and extrusion. A noticeable weight loss was observed slightly above 150 °C associ ated with degradation of the polymer matrix, likely scission and decomposition of the perfluorinated alkyl tail to yield an alkene or alcohol [19,20]. Complete degradation of the polymeric matrix was achieved by *ca.* 400 °C for each composite studied. The resid ual mass observed at 500 °C was used to determine the particle content of the composite. Figure 2 contains an overlay of the TGA curves for the respective composites along with a chart illustrating the difference in the observed particle content from the initial par ticle loadings used to prepare the composites. Based upon the TGA results it was clear that the *in situ* polymerization approach



Scheme 1. Schematic representation illustrating the synthesis of AlFA composites.

Fig. 1. As-processed and machined (left to right) AlFA-0, AlFA-10, AlFA-30, AlFA-50 and AlFA-60 nanocomposite specimens, 4 mm dia. × 8 mm long.



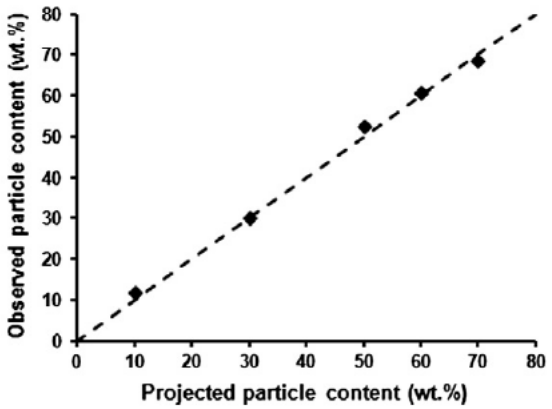


Fig. 2. (a) TGA overlay of AlFA composites illustrating polymer degradation and residual particle content. (b) Experimentally observed composite particle content determined from TGA analysis. The dashed line represents the projected particle content.

Table 2
Summary of the thermal analysis data obtained for the AlFA composite series.

Composite	Wt.%	Vol.%	T_m (°C)
AlFA-0	0	0	83.5
AlFA-10	12.0	7.47	84.5
AlFA-30	30.1	20.3	85.5
AlFA-50	52.7	39.8	84.0
AlFA-60	60.9	48.0	87.0
AlFA-70	68.7	56.5	85.5

utilized to prepare the AlFA composites allowed for accurate control over the amount of particles that were directly incorporated into the polymer matrix.

DSC analysis was also performed on the composites to determine the melting temperature (T_m) as an indicator towards the processability of the composite materials. Remarkably, these materials did not display any significant loss in their thermoplastic behavior, even at high particle loadings. Because the nano Al surface has been previously functionalized with a methacrylic monomer that is capable of reacting with the growing poly(PFDMA) chains during polymerization, one might anticipate that the functionalized nano Al would act as a crosslinker as it has the potential to react with multiple propagating chains simultaneously due to the high surface coverage of monomer and the 3 dimensional, spherical architecture of the particles. However, the thermal analysis data does not support this theory since there is not a significant increase (or decrease) in the T_m or thermal stability (decomposition temperature) of the materials as would be expected for a highly crosslinked polymer. This result suggests the use of conventional polymer processing techniques, such as melt extrusion, can be utilized to consolidate and shape the composites even at high particle loadings. The thermal analysis results obtained from both TGA and DSC are summarized in Table 2.

3.1. Microstructural analysis

Both the mechanical properties and reactivity of the composites are dependent on the interface between the polymer matrix and the nano Al filler. We prepared TEM specimens of each composite in order to characterize the particle polymer interface and microstructure as a function of particle content, as displayed in Fig. 3. In this system, reactivity is derived from the interaction (reaction) of the nano Al with fluorine atoms found within the polymer matrix as described in Eq. (1); increasing intimacy between the two components should increase the reactivity of the material. Additionally, stress transfer from the polymer matrix into the nano Al filler also requires an intimate chemical and/or mechanical interaction

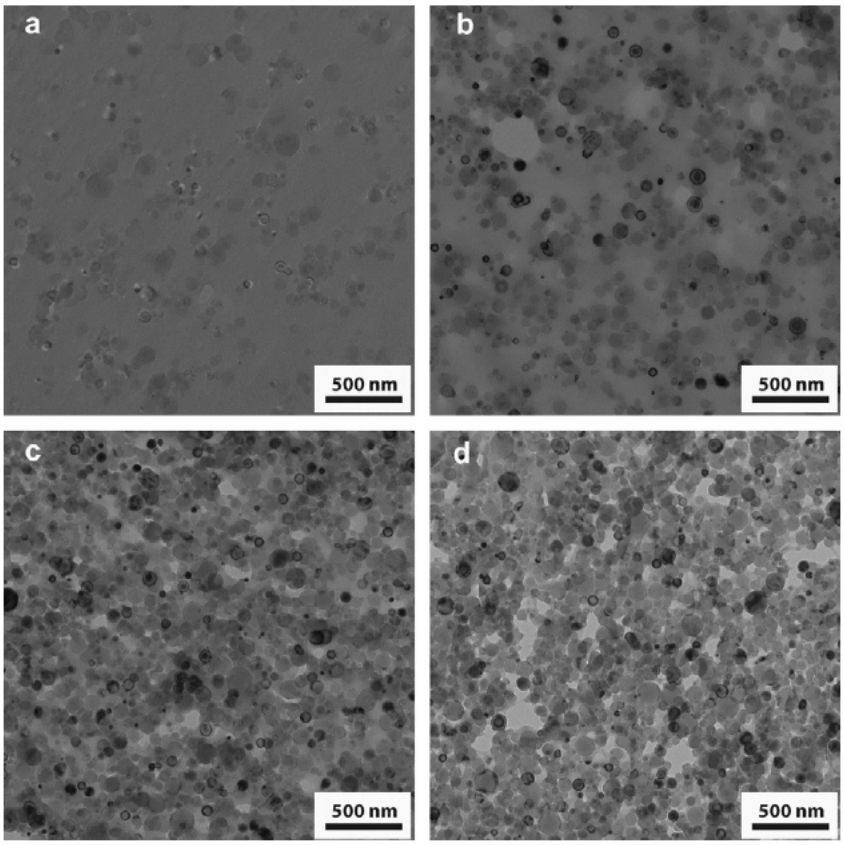


Fig. 3. TEM micrographs obtained from cross-sections of (a) AlFA-10, (b) AlFA-30, (c) AlFA-50 and (d) AlFA-60 composites.

between the two. Intimate mixing of particles with the polymer matrix is clearly evident from the micrographs. There are no visible signs of particle matrix decohesion, suggesting that the interface is continuous and that the PAM layer on the oxide surface has be come integrated within the polymer matrix, as thought. Although many of the particles appear to be dispersed in a discrete non aggregated form, some aggregation still appears to be present even after compounding and extrusion. The AlFA 10 and AlFA 30 com posites displayed small areas of aggregation but for the most part the particles appear to be homogeneously dispersed throughout the matrix. Moreover, there appear to be very few voids present within the sample; a proportion of the voids that are observed in Fig. 4a and b, are considered artifacts from TEM sample prepara tion, such as particle pullout or matrix tearing during microtomy. Aggregation was present in the consolidated AlFA 50 and AlFA 60 composites, however, it is difficult to distinguish from the ma trix due to the high particle loadings. The amount of porosity in the composite materials also increased with the higher particle load ings; Fig. 3c and d show voids within aggregates that were not pen etrated by monomer or polymer during polymerization or compounding and extrusion. We anticipate that these aggregates will have little effect on reactivity since they are loosely packed and maintain high surface area. Conversely, voids within the ma trix will have an effect on the overall composite density, and there fore could negatively affect mechanical strength. Theoretical maximum densities (TMDs) were calculated for the 8 mm long × 4 mm dia. pellets and ranged from 99% for the neat polymer to 88% and 94% TMD for the AlFA 50 and AlFA 60 composites, respectively.

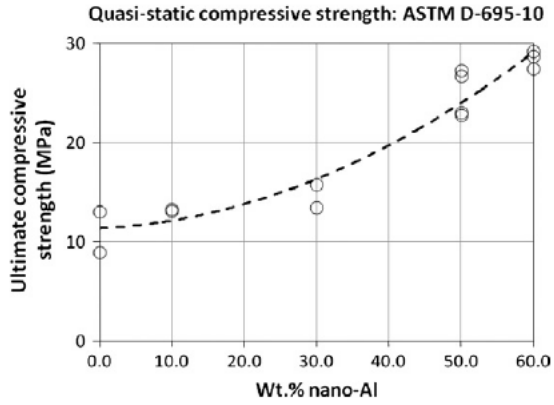


Fig. 4. Quasi-static compressive strength (σ_c^u) measured as a function of nano-Al content for AlFA nanocomposites, according to ASTM D-695-10. Dashed curve is an aid for the eye.

3.2. Compressive strength

It was hypothesized that the compressive mechanical proper ties of the AlFA materials would be superior to the neat polymer due to the high particle loadings and also the direct chemical bond ing between the nano Al and the polymer matrix. The neat poly mer (AlFA 0) displayed a peak compressive strength of *ca.* 11 MPa. The addition of PAM functionalized particles into the poly mer matrix resulted in an increase in compressive strength, with the highest values, *ca.* 25 28 MPa, obtained for the AlFA 50 and 60 composites. Figure 4 is a plot showing measured ultimate compressive stress as a function of nano Al content.

3.3. Combustion dynamics of AlFA composites

In addition to understanding the mechanical behavior of nano Al/fluoropolymer composites, one of the goals of the research was also to investigate the reactive properties of these materials.

Semi quantitative combustion rate experiments were performed by igniting a cylindrical pellet (8 mm long × 4 mm dia.) at each composition with a small butane flame and allowing the pellets to burn open to lab air. The combustion events were recorded with a digital high speed color video camera operating at 3000 frames per second. Figure 5 shows the evolution of the measured intensity of the video images as a function of time for the AlFA 30, AlFA 50 and AlFA 60 materials accompanied by a time sequence of full color images obtained from the combustion respective composites.

All of the composites, with the exception of AlFA 0 and AlFA 10, demonstrated a self sustaining deflagration upon ignition. Since the AlFA 0 composite did not contain any nano Al, the pellet sim ply melted upon heating. The AlFA 10 composite also initially melted but subsequently ignited after sustained heating. This could occur due to the loss of polymer as smoke and char until the nano Al becomes concentrated enough to sustain a reaction.

In contrast, ignition of the AlFA 30 pellet occurred immediately upon contact with the flame. A self sustaining intense white yellow flame was observed accompanied by the production of a significant amount of smoke and black char. The char was col lected and analyzed by XRD (Fig. 6) to determine the identity of the solid products. The primary component of the char was AlF_3 indi cating that nano Al was indeed reacting with the fluorinated poly mer matrix in a similar manner to PTFE. Other products also present in the char included aluminum oxide, unreacted metallic aluminum (presumably ejected during the rapid burning), alumi num carbide (Al_4C_3) and aluminum oxide carbide although these two products were minor compared to AlF_3.

Combustion of the AlFA 50 pellet yielded the most intense and rapid reaction, compared to the other composite compositions. The pellet ignited readily upon exposure to the butane flame producing an intense yellow orange flame that rapidly consumed the entire pellet releasing smoke and gasses which physically moved the pel let across the wire gauze as it burned. The intensity plot in Fig. 5 shows two distinct peaks, one around 500 ms and another around 1.0 s, with the deflagration process requiring around 1.3 s for

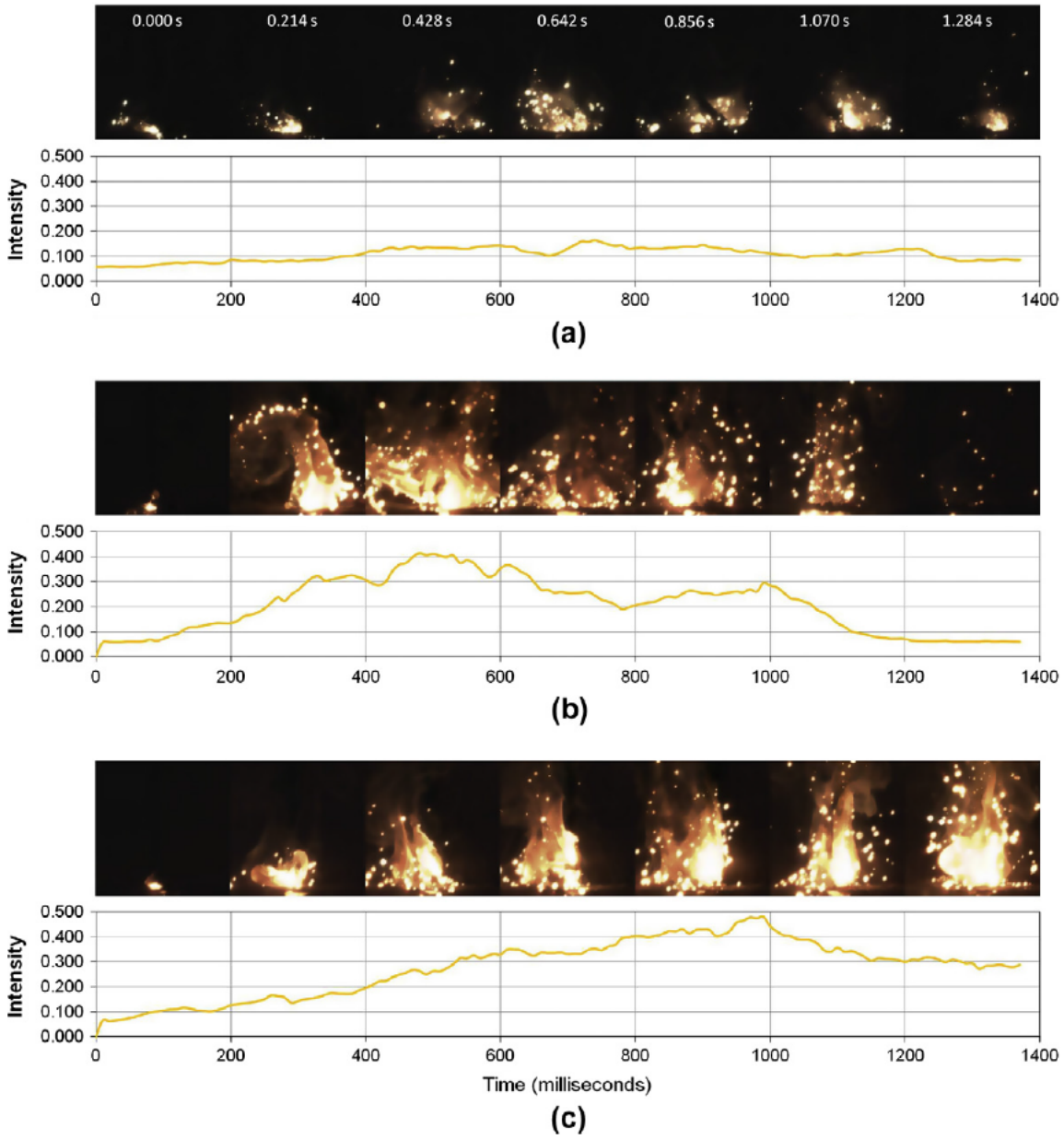


Fig. 5. Plot showing measured reaction intensity for (a) AlFA-30, (b) AlFA-50, and (c) AlFA-60 composites, based on high-speed digital video images of combusting pellets, as a function of time.

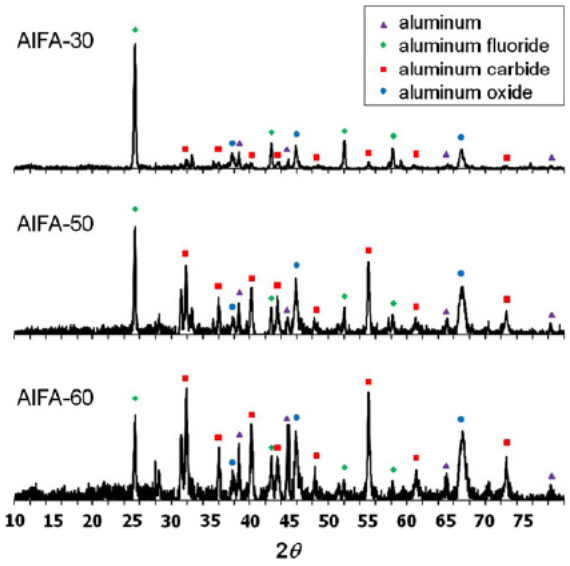


Fig. 6. XRD patterns obtained from the soot collected after completion of the combustion experiments performed on the respective AlFA composites.

complete combustion. The char obtained as a product of the reaction was black and gray in color. XRD analysis again confirmed the presence of AlF_3 as the major product, but also the Al_4C_3 and aluminum oxide peaks were more prevalent than was observed for the AlFA 30 char. Residual aluminum and aluminum oxide carbide were also present but only as trace phases.

Ignition and deflagration of the AlFA 60 pellet was slower than the AlFA 50 pellet. A similar yellow orange flame was produced, which steadily grew in intensity as the reaction progressed. A total reaction time of more than 1.5 s was required to obtain complete combustion of the pellet with the most intense flames appearing *ca.* 1.0 s after ignition. The char product was primarily a dark gray color. XRD analysis confirmed Al_4C_3 as the major component of the char followed by AlF_3 and aluminum oxide; residual aluminum was also present as a trace phase.

The stoichiometric reaction between nano Al and PTFE resulting in AlF_3 and carbon (as previously shown in Eq. (1)) requires a composition equivalent to 26.5% Al and 73.5% PTFE by weight as shown in the following equation:

$$26.5\%Al + 73.5\%(-CF_2-)_n \rightarrow 82.4\%AlF_3 + 17.6\%C \quad (2)$$

TGA oxidation studies confirmed that the nano Al used in the AlFA composites has an 80% active aluminum content due to the presence of an inert oxide shell, therefore 20% of the nano Al mass does not contribute anything to the reaction. Moreover, the poly(PFDMA) fluoropolymer contains *ca.* 60% fluorine by mass, compared to 75% for PTFE. Adjusting the stoichiometry of Eq. (3) to account for both these factors results in a stoichiometric composition for complete fluorination equivalent to 26.5% nano Al in 73.5% poly(PFDMA) fluoropolymer by weight as shown in the following equation:

$$26.5\%\ \text{nano-Al} + 73.5\%\ \text{poly(PFDMA)} \rightarrow 78.0\%AlF_3 + 16.70\%C + 5.3\%Al_2O_3 \quad (3)$$

The preceding analysis provides a thermodynamic basis for AlF_3 being the dominant product in the soot collected from the AlFA 30 combustion, since the AlFA 30 composition is very close to the stoichiometric condition required for complete fluorination. Moreover, AlFA 30 being slightly fuel rich leaves a small residual amount of aluminum available to react with oxygen and/or carbon to yield the observed oxide and/or carbide products (Eqs. (4) and (5)), respectively.

$$4Al + 3O_2 \rightarrow 2Al_2O_3, \quad \Delta H^0 \quad 3351.44\ \text{kJ} \quad (4)$$

$$4Al + 3C \rightarrow Al_4C_3, \quad \Delta H^0 \quad 205.99\ \text{kJ} \quad (5)$$

Since the open burn testing was carried out in air, it is possible that both oxidation and fluorination mechanisms can make contributions towards the overall energetic performance of the material therefore it is possible to optimize the material for both reactions by combining Eqs. (1) and (4) as shown below in Eq. (6). Once again accounting for the active aluminum and fluorine available in nano Al and poly(PFDMA), respectively, Eq. (6) can be easily translated into Eq. (7).

$$6Al + 3(-CF_2-)_n + 3O_2 \rightarrow 2Al_2O_3 + 2AlF_3 + 3C, \quad \Delta H^0 \quad 3943.42\ \text{kJ} \quad (6)$$

$$41.7\%\ \text{nano-Al} + 38.6\%\ \text{poly(PFDMA)} + 19.7\%O_2 \rightarrow 48.6\%Al_2O_3 + 42.4\%AlF_3 + 9.0\%C \quad (7)$$

Examination of Eq. (7) indicates that a composition equivalent to 51.9% nano Al and 48.1% poly(PFDMA) by weight is required for optimization of both fluorination and oxidation. The AlFA 50 composition prepared for this work is very close to this stoichiometric composition and it was also the most reactive composite in combustion tests, requiring the shortest overall time to achieve complete deflagration and producing the most intense overall flame (see Fig. 6). We propose that the increased performance of the AlFA 50 composite, compared to the other AlFA composites, is due to its proximity to near stoichiometric conditions. Enough aluminum was present in the composite to support simultaneous oxidation and fluorination which produces a significant amount of heat that further accelerates diffusion between the reacting species thereby increasing the rate of reaction. Furthermore, an additional amount of energy equivalent to a maximum of 1180.50 kJ can be released by combustion of the carbon produced as a byproduct of the fluorination event.

A significant increase in the formation of Al_4C_3 was observed in the AlFA 60 composite compared to the others, although some Al_4C_3 was present in the AlFA 50 soot. The mechanism(s) for carbide formation are still unclear but is anticipated to occur through reaction of the aluminum with carbon, (Eq. (5)).

The carbon required to produce the carbide must come from the polymer, either in the methacrylate backbone or from carbon produced during fluorination. In the AlFA 60 composite, specifically, the composition is fuel rich with more than enough aluminum present to support fluorination and oxidation as well as carburization. Additionally, because the carbon produced from fluorination is also responsible for carbide formation then Eq. (8) is obtained which is readily translated into Eq. (9) after accounting for the active aluminum in nano Al and available fluorine in poly(PFDMA).

$$10Al + 3(-CF_2-)_n + 3O_2 \rightarrow 2Al_2O_3 + 2AlF_3 + Al_4C_3, \quad \Delta H^0 \quad 4149.41\ \text{kJ} \quad (8)$$

$$54.3\%\ \text{nano-Al} + 30.2\%\ \text{poly(PFDMA)} + 15.5\%O_2 \rightarrow 37.2\%AlF_3 + 33.8\%Al_2O_3 + 29.0\%Al_4C_3 \quad (9)$$

This corresponds to a composition of 64.3% nano Al and 35.7% poly(PFDMA) which is near the AlFA 60 composition tested in this work. Notably, the formation of an Al_4C_3 phase ((ΔH_F (Al_4C_3) =

205.99 kJ/mol)[11] does not contribute significantly to the over all energetic release, since it provides only 1.88 kJ per gram of aluminum.

Deviations towards fuel lean compositions result in loss of reac tivity as was observed by the lack of reaction for the AlFA 10 com posite. Particle contents closer to the stoichiometric conditions for fluorination yet slightly fuel rich, such as the AlFA 30 composite, resulted in near complete reaction between the nano Al and the fluorinated matrix, with only minor phases present in the reaction products indicating both air oxidation and/or carbide formation. Since these reactions occurred in the presence of air, the preva lence of AlF_3 as the dominant product of AlFA 30 combustion sug gests that fluorination is kinetically favored over oxidation even though formation of the oxide is thermodynamically preferred. However, as the composition is adjusted to fuel rich conditions AlFA 50 and AlFA 60 the oxide and carbide products grow rap idly accompanied by a decrease in AlF_3. These compositions are fluorine deficient and therefore air oxidation (Eq. (4)) can compete with fluorination (Eq. (3)) and eventually becomes the dominant mechanism for aluminum consumption after the all of the fluorine has been consumed. This is supported by the intensity profiles found in Fig. 5. It is postulated that the first peak in the AlFA 50 data is due to the kinetically faster fluorination reaction (or a com bination of fluorination and oxidation), and the second peak (around 1.0 s) is due solely to the oxidation of the remaining alu minum, with both reactions contributing towards the overall intensity. Moreover, if carbide is formed as a product from the reaction of nano Al with carbon produced during the initial fluori nation (Eq. (5)), then this explains why the carbide phase is only present in the fuel rich mixtures since fluorination is kinetically preferred and completely consumes the aluminum under near stoi chiometric conditions for fluorination (AlFA 30) leaving no alumi num available to react with the carbon.

By numerically integrating the total area under the intensity time curves, one can obtain a simple, semi quantitative measure of the extent of reaction. When this is done, it shows that the total integrated intensity scales linearly with the amount of nano Al present in the composite, Fig. 7.

This would be expected on the basis that combustion is occur ring in air, i.e. with unlimited supply of oxidizer either F or O from the fluoropolymer or O from the atmosphere. Also plotted on this figure is the elapsed time from ignition to peak intensity, i.e. the deflagration time, taken from the data in Fig. 5. This gives a semi quantitative measure of the kinetics of the combustion reaction, as a function of composition. There is a minimum in the deflagration time that corresponds to the AlFA 50 composition, i.e. this composition has the highest overall burn rate. We postu late that this occurs because the AlFA 50 composition was nearest to the stoichiometric conditions for both fluorination and oxidation thereby providing multiple reaction pathways for consumption of the aluminum. The large plume present during combustion sug gests that aluminum is being ejected from the pellet or vaporizing and is reacting in air accompanied by the combustion of the carbo naceous byproducts from the polymer and the carbon produced during fluorination. These events provide additional heat to the system thereby enhancing the overall burn rate for that composi tion. Additionally, the adiabatic flame temperature for oxidation of aluminum is approximately 550 °C hotter than the adiabatic flame temperature for fluorination, therefore one would expect the AlFA 50 combustion to occur faster than the pure fluorination observed in the AlFA 30 composition since the higher tempera tures produced during combustion will enhance the overall rate of reaction. Similar observations have been reported for magne sium/Teflon/Viton composites [10]. By the same arguments, the AlFA 60 product takes longer to react because more aluminum is consumed through air oxidation and carbide formation due to the lack of fluorine present in the composition. These reactions are kinetically slower than fluorination and formation of the car bide, although exothermic, produces much less heat than combus tion of the carbonaceous byproducts. Therefore less heat is produced to enhance the overall burn rate and a slower burn time is observed. Additionally, in order for oxygen to react with particles at the interior of the pellet the oxygen must diffuse through the surface of the pellet into the core. Since more of the pellet is com prised of aluminum more oxygen is needed to fully consume the aluminum which results in an overall slower reaction time.

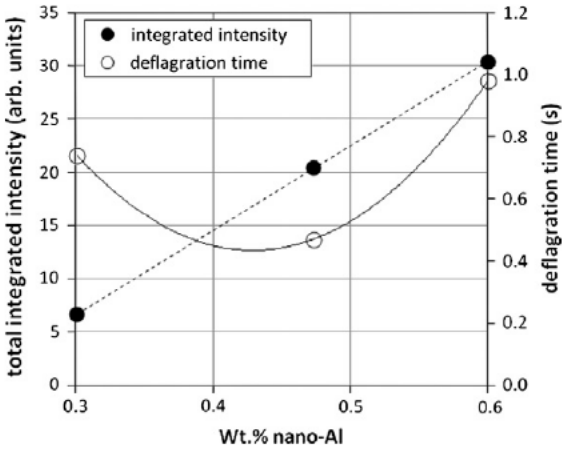


Fig. 7. Total integrated intensity (area under curves from Fig. 5; filled symbols) and deflagration time (time taken to reach peak intensity; open symbols) plotted vs. composition, for open-burn combustion testing of AlFA composites.

4. Conclusion

We have developed a new approach toward the preparation of reactive nano Al/fluoropolymer composites utilizing an *in situ* free radical solution polymerization of PFDMA in the presence of PAM functionalized nano Al. The resulting AlFA composite materi als have been prepared with nano Al loadings of 10%, 30%, 50%, 60% and 70% by weight, while composites with 60 wt.% nano Al or less exhibited thermoplastic behavior and are capable of being pro cessed through melt extrusion. Chemical integration of the nano Al particles into the fluoropolymer matrix results in a continuous phase at the particle polymer interface which was shown to en hance the mechanical performance of the material.

Open air combustion experiments performed on consolidated (extruded) pellets initiated by exposure to a butane flame resulted in a self sustaining deflagration for the AlFA 30, AlFA 50 and AlFA 60 composites. Combustion of the AlFA 30 composite primarily resulted in the formation of AlF_3 as it was nearest to the stoichiom etric reaction conditions for fluorination. However, since these experiments were performed open to air, combustion of the AlFA 50 composite yielded the most energetic response (minimum time for complete deflagration) as the aluminum content was high enough to allow for multiple reaction pathways including fluorina tion, oxidation and carburization.

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