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**SYNTHESIS AND REACTIVITY OF NANO-
ALUMINUM/ZONYL[®] TM FLUOROPOLYMER
COMPOSITES (PREPRINT)**

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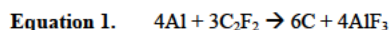
SYNTHESIS AND REACTIVITY OF NANO-ALUMINUM/ZONYL[®] TM FLUOROPOLYMER COMPOSITES

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Introduction

Fluorinated polymers have gained increasing attention as reactive oxidizing materials for energetic formulations over the past two decades. Specifically, reactions between aluminum, silicon, and/or magnesium with poly(tetrafluoroethylene) (PTFE or Teflon[®]) and Viton[®], a copolymer of poly(vinylidene fluoride) and poly(hexafluoropropylene), have been well documented in the literature.^{1,2} Though the highly fluorinated nature of these polymers yields a chemically inert material with low friction resistance and non-adhesive properties the fluorinated byproducts produced during the decomposition of these polymers are highly reactive with the previously mentioned metals. For example, the reaction of Al with PTFE to yield AlF₃ (Equation 1) liberates nearly twice the energy per gram (-13.5 kcal/g) than combustion of Al with oxygen to yield Al₂O₃ (-7.4 kcal/g).³



Typically composites prepared from these reactive mixtures are done so by powder compaction with the most reactive composites being comprised of both nano-sized metal and fluoropolymer powders. Unfortunately, this technique does not produce any direct bonding between the surfaces of the metal particles and polymer beads therefore the materials properties, such as compressive strength, are expected to be rather poor. Herein we report a new approach towards the preparation of reactive fluoropolymer nanoparticle composites utilizing chemical functionalization of aluminum nanoparticles (nano-Al) followed by an *in situ* polymerization of a commercial fluorotelomer mixture in the presence of the functionalized particles. This process yields a reactive solid composite material with thermoplastic behavior that is amenable to conventional composite processing techniques.

Experimental

Materials. Aluminum nanoparticles (80 nm, 80% active Al content) were obtained from Novacentrix, Inc. and were stored under argon in a glove box (O₂ ≤ 1 ppm; dew point = -80 °C) prior to use. Zonyl[®] TM fluorotelomer and 2-carboxyethylacrylate (CEA) and were acquired from Aldrich and used as received. Cyclohexanone (Aldrich) was dried over CaH₂ and distilled prior to use. 2,2'-azobis(2-methylpropionitrile) (AIBN) (Aldrich) was recrystallized from acetone prior to use.

Instrumentation. Thermogravimetric analysis (TGA) was performed on a TA Instruments SDT Q600 dual TGA/DTA. Samples (5 to 20 mg) were placed into a tared alumina crucible with an empty alumina crucible 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.

High resolution transmission electron microscopy (HR-TEM) images were acquired on a FEI Titan HR-TEM with a CS corrector at an operating voltage of 300 keV. Samples were prepared using a microtome to remove 70 nm thick slices of the material which is placed onto a copper grid for imaging.

Combustion experiments were performed by rapidly heating a 0.25" diameter by 0.25" long cylindrical pellet with a propane/oxygen flame on a firebrick under a fume hood. Combustion was recorded using a digital camcorder at 30 frames per second.

Synthesis of nano-Al/Zonyl[®] TM fluoropolymer composites. The procedure used for the surface functionalization of nano-Al with CEA prior to composite formation has been reported in a previous literature reference.⁴ A typical polymerization for the preparation of 30 wt.% nano-Al/Zonyl[®] TM fluoropolymer composite 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 CEA-co-nAl (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 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. Stirring was started at 235 rpm and the reaction vessel was submerged into an external oil bath at 75 °C and held for 4 hours. In most cases polymerization was completed prior to 4 hours and could be observed by an increase in viscosity and precipitation of the composite from the solvent, however, the reaction was still held at temperature for 4 hours to ensure the polymerization was complete. After 4 hours the heat was removed and the reaction was allowed to cool to room temperature. The composite was scraped out of the reaction vessel, transferred to a filtration apparatus fitted with a 0.2 μm PTFE membrane and washed with acetone to remove cyclohexanone and any unreacted monomer. The filtered product was then dried in a vacuum desiccator to remove residual solvent. Reactions yields between 90-95% were observed for each composite.

To ensure uniform distribution of the CEA-co-nAl throughout the material each composite was compounded for a minimum of 3 minutes in a DACA Instruments benchtop twin-screw extruder at 150 °C. The compounded material was then extruded into a cylindrical die into a copper clam-shell mould and allowed to cool. The final product was a gray, waxy solid with variable metallic luster depending on particle content. (Metallic luster increased as particle content was increased).

Results and Discussion

Zonyl[®] TM fluorotelomer is a mixture of perfluorinated alkyl methacrylates with an average molecular weight of 534 g/mol. The mixture displays an average fluorine content of 60 %, which is less than PTFE (75%). Fluorine content is lost due to the methacrylate subunit of the monomer. The perfluorinated alkyl chains that are attached to the methacrylate subunit are comprised of -(CF₂)_n- units, where n = 5, 7 or 9, along with a terminal -CF₃ unit. The perfluoroalkyl chains are essentially short chain oligomers that mimic PTFE; therefore we expect the polymer to have similar reactivity towards metal powders. Unlike PTFE, the mixture of monomers found in Zonyl[®] TM is active towards conventional free radical polymerization and yields a polymer that is a solid at room temperature and displays thermoplastic behavior.

Utilizing an *in situ* polymerization approach, Figure 1, we have prepared a series of nano-Al/ Zonyl[®] TM fluoropolymer composites with particle contents ranging from less than 20 wt.% to 34.5 wt.%, Figure 2. The materials produced display thermoplastic behavior, even up to a 34.5 wt.% particle loading, and are easily processed using conventional polymer processing techniques such as extrusion. Chemical functionalization of the nano-Al surface with CEA prior to polymerization and composite formation provides direct chemical bonding of the polymer matrix to the nano-Al particles embedded within, resulting in an intimate connection between the polymer matrix and the particles, as can be observed in the TEM micrographs found in Figure 3. This type of direct bonding to the particle is not achieved in any of the PTFE/Viton/metal particle composite systems that have been currently studied and it is our hypothesis that this direct bonding could potentially increase the overall strength of the composite materials. We are currently undergoing investigations to study the validity of this hypothesis.

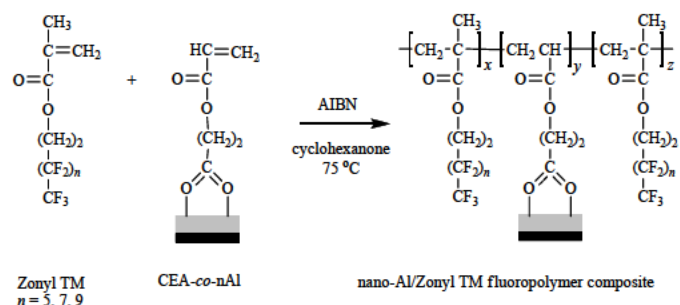


Figure 1. Reaction scheme for the synthesis of nano-Al/ Zonyl[®] TM fluoropolymer composites.



Figure 2. Picture displaying the extruded nano-Al/ Zonyl[®] TM fluoropolymer composite at a) less than 20 wt.%, b) 22.5 wt.% and c) 34.5 wt% nano-Al content.

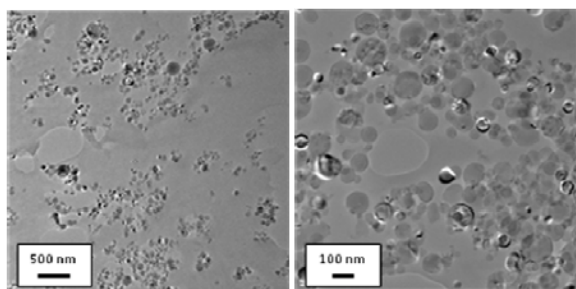


Figure 3. TEM micrographs displaying the microstructure of the 22.5 wt.% nano-Al/ Zonyl[®] TM fluoropolymer composite.

Thermal analysis performed on the composite materials indicates that the polymer begins to degrade above 200 °C with degradation complete by 400 °C under both argon and air atmospheres. In the presence of oxygen the composites combust around 320 °C, well below the melting point of Al or the combustion onset temperature for nano-Al/PTFE. In order to determine if the presence of fluorine was indeed contributing to the reactivity of our composites we prepared a non-fluorinated analog comprised of 22.5 wt.% nano-Al in poly(methyl methacrylate) (PMMA). Pellets were prepared from both materials, placed directly onto a firebrick and were rapidly heated with a propane/oxygen flame, **Figure 4**. A visibly more violent response was observed from the 22.5 wt.% nano-Al/ Zonyl[®] TM fluoropolymer composite confirming that the fluorinated polymer matrix does indeed contribute to the reactivity of the material.



Figure 4. Combustion experiments performed on a) 22.5 wt.% nano-Al/PMMA and b) 22.5 wt.% nano-Al/ Zonyl[®] TM fluoropolymer composite material.

Conclusions

We report the synthesis of a novel nano-Al/fluoropolymer composite comprised of CEA functionalized nano-Al in a Zonyl[®] TM fluoropolymer matrix prepared by *in situ* free radical polymerization. The resulting composites were prepared with particle loadings ranging from less than 20 wt.% up to 34.5 wt%. All of the materials demonstrated thermoplastic behavior and were able to be processed through twin-screw extrusion. Qualitative combustion studies indicate that the fluorine present in the Zonyl[®] TM fluoropolymer matrix does indeed contribute to the reactivity of the materials.

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