

## **Novel Processing to Produce Polymer/Ceramic Nanocomposites**

Joe Spencer, Alan Weimer, Steve George, Karen Buechler, John Ferguson, University of Colorado  
Department of Chemical and Biological Engineering

### **Abstract**

An innovative process to incorporate ceramic with polymer has been identified. Using atomic layer deposition (ALD), an extremely thin 10 nanometer film of alumina is deposited onto high density polyethylene particles. These particles can then be extruded, during which the ceramic shells break up and disperse throughout the polymer. This method circumvents the difficulties of intimate blending of ceramics and polymers. ALD can also potentially be used to deposit other films with minimal loading for applications like conductive polymers. The film coating also changes the fluidization properties of the polymer powder.

### **Introduction**

Polymer materials can be greatly affected by nanoscopic inclusions of ceramic material. These inclusions can result in increased impact, thermal, and flame resistance as well as decreased permeability. Work has primarily been done with nanoscopic montmorillonite clay, the inclusion of other ceramics has not been deeply investigated. Alumina is the focus of this study and provides a number of benefits over montmorillonite.

Difficulty is often encountered when trying to blend and mix a ceramic with a polymer, so a novel application of atomic layer deposition (ALD) is used. The ALD process places thin alumina films directly on the surface of 30 micron polyethylene particles. The particles can then be extruded with existing heated methods and the alumina films become dispersed in the polymer. By incorporating the film directly onto the polymer blending complications observed with clay fillers are avoided.

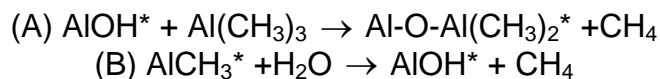
ALD also has a number of advantages over conventional deposition methods. Chemical Vapor Deposition (CVD) is one of the most prevalent surface coating techniques but requires operating temperatures over 300°C, which is much higher than the melting point of the polymer. Plasma enhanced CVD can aid in lowering the operating temperature, but introduces high energy particles which can damage the polymer substrate. A sputtering technique may also be employed at an acceptable temperature, but is a line of sight technique and cannot coat a particle evenly.

### **Background**

The incorporation of nanoparticles into polymers can significantly affect their physical properties, resulting in mechanical<sup>i</sup>, diffusion barrier, and flame retardant<sup>ii</sup> improvements. An order of magnitude increase in the strain to failure strength of polymethyl methacrylate is observed when just 5% by weight of alumina is added<sup>iii</sup>. Uniformity in nanocomposites is difficult to achieve with normal blending techniques. A novel way to promote intimate mixing is to coat polymer particles with alumina via atomic layer deposition (ALD). When these coated particles are extruded, the alumina shells are crushed in the extrusion process and become well mixed with the bulk of the polymer.

High-density polyethylene (HDPE) is a widely used polymer and a good candidate for experimentation. Polyethylene and alumina are also biocompatible. Combining these two materials could make a stronger polymer with many potential biomedical applications. Along with the typical arthroplasty applications seen for polyethylene, successful biocompatibility has recently been observed for an alumina-polyethylene blood pump<sup>iv</sup>.

To encase HDPE particles with alumina, atomic layer deposition is used. ALD is a surface chemistry technique which splits chemical vapor deposition reactions into binary half-reactions. For alumina chemistry, trimethylaluminum (TMA) and water combine to create the half-reactions (A) and (B) where asterisks indicate surface species<sup>v,vi</sup>.



The half-reactions are dosed in an A-purge-B-purge cycle with each reactant admitted into the reactor separately. After the TMA for reaction A enters the system for a desired dosing time, a purge gas is used to remove excess reactant from the environment before the precursor for reaction B, H<sub>2</sub>O, enters. A purge step follows the B half-reaction, ending a complete cycle. The aforementioned mechanism applies only to substrates with preexisting hydroxyl groups on the surface.

ALD alumina chemistry has been performed on a variety of materials, with a semiconductor motivated emphasis on silicon. Most materials with a native oxide surface will coat well with the established ALD chemistry. However, polyethylene has no native hydroxyl groups on the surface to react; therefore the alumina film must begin growing in some other manner. While work on coating polyethylene has yet to be published, it has been observed in other polymers that the reactants may interact with the substrate in an unpredicted manner<sup>vii</sup>.

Alumina ALD on a polymer called SiLK (trademark of Dow Corning) has been successfully performed. While this polymer is not chemically identical to HDPE, it also lacks necessary hydroxyl functional groups. A mechanism has been suggested through observations that TMA adsorbs onto the surface and then diffuses into the SiLK polymer. It is suspected the TMA may even dissolve into the SiLK polymer. When water reacts with this imbedded TMA, small alumina clusters form within the polymer. These nucleated clusters then support the film growth by allowing ALD to continue on AlOH\* termination sites.

Another proposed method for film growth on SiLK is due to diffused moisture. Because water diffuses into the polymer at relatively low humidity, it is possible that TMA reacts with water near the surface. This would form small alumina clusters. The film would then be able to grow using the method previously mentioned.

Data collected from experiments with SiLK support these theories. A profilometer was used to measure the uniformity and average thickness of the alumina coating on the SiLK polymer. These measurements indicated no growth before 23 A-B cycles. This is expected if the preliminary cycles are diffusing and reacting within the surface. If such a phenomenon is occurring, quartz crystal microbalance (QCM) measurements should indicate a mass gain during these initial cycles. A QCM was used to record the mass change during deposition in situ, and the results support the adsorption theories. Significant gains in mass were seen

during the initial cycles. These gains can be related to alumina film growing within pores of the polymer, or nucleation within the polymer. If either is the case, the growth rate will be faster during this pore filling/nucleation phase than during the lower surface area monolayer film deposition phase. The growth rate seen from the QCM data is higher than average during approximately the first 20 cycles. After this time, the growth rate is extremely linear, further suggesting monolayer deposition. While HDPE may not behave exactly like the SiLK polymer, these results may help to explain observations made for atomic layer deposition on HDPE.

## Methods

The high density polyethylene particles are coated using a fluidized bed reactor to ensure the exchange of surface contact points and even distribution of the precursors. A porous metal frit is used as the distributor plate instead of a traditional perforated plate. The fluidized bed features a disengaging zone which houses 4 metal filters that have the same porosity as the frit. The reactor is 2.5 inches in diameter in the fluid bed area and 4" in diameter in the disengaging/filter area. Fluidization is also vibration assisted by two Martin Engineering industrial vibration motors.

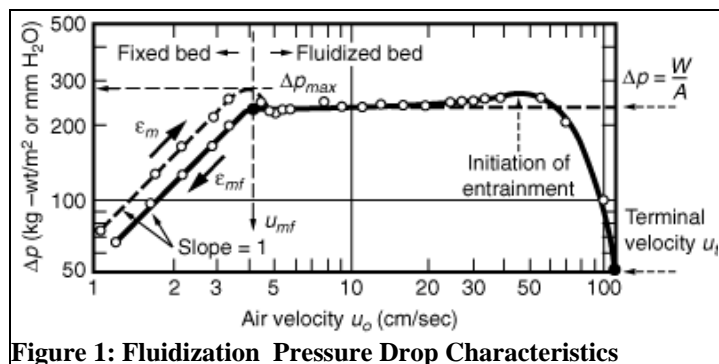


Figure 1: Fluidization Pressure Drop Characteristics

To examine fluidization at low pressure, the pressure drop over the bed is recorded for a range of gas flow rates. The data for the bed without powder is subtracted from the data for the bed with powder. This gives the pressure drop resulting from the bed powder alone. Figure 1 shows the pressure curve observed for a fluid bed. The pressure drop across the distributor in a fluid bed will plateau at the minimum fluidization velocity. This behavior can be reproduced with the polyethylene in the fluidized bed, as in Figure 2. The minimum fluidization velocity occurs with 12-13 SCCM of nitrogen flowing through the system.

Reactions were carried out at pressures equal to or less than 2 torr and a bed mass of 100 grams. The TMA was emitted into the chamber in 50 second doses, which equate to approximately  $8 \times 10^{-4}$  moles, twice the stoichiometric amount necessary to coat each particle with 1.1 Å of alumina. The system then underwent a 70 second purge of nitrogen. Water was then dosed for 30 seconds. The higher vapor pressure of water allowed for shorter dose times with the same amount of exposure. The water dose was also more than double the stoichiometric amount needed for the alumina film.

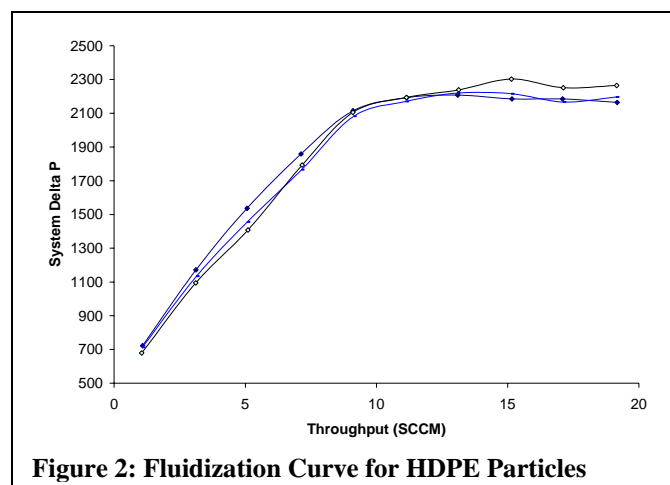
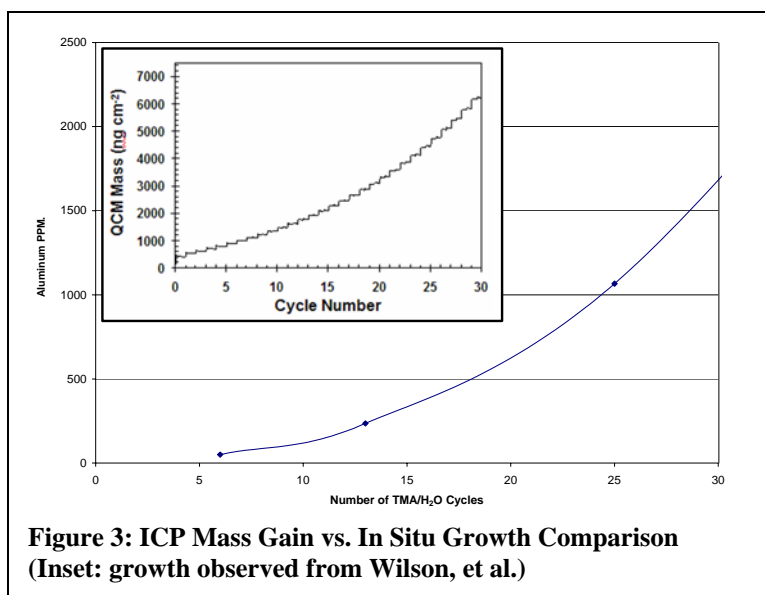


Figure 2: Fluidization Curve for HDPE Particles

Experiments were performed for coatings of 6, 13, 25, 50 and 100 cycles. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to analyze aluminum content on the polyethylene particles. ICP-AES provides a parts per millions by mass of aluminum in relation the powder. Exact part per million counts vary between batches, but trends are qualitatively dependable within each batch.

The coated powder was extruded in a custom, bench-size, Bonot heated extruder at 175°C.

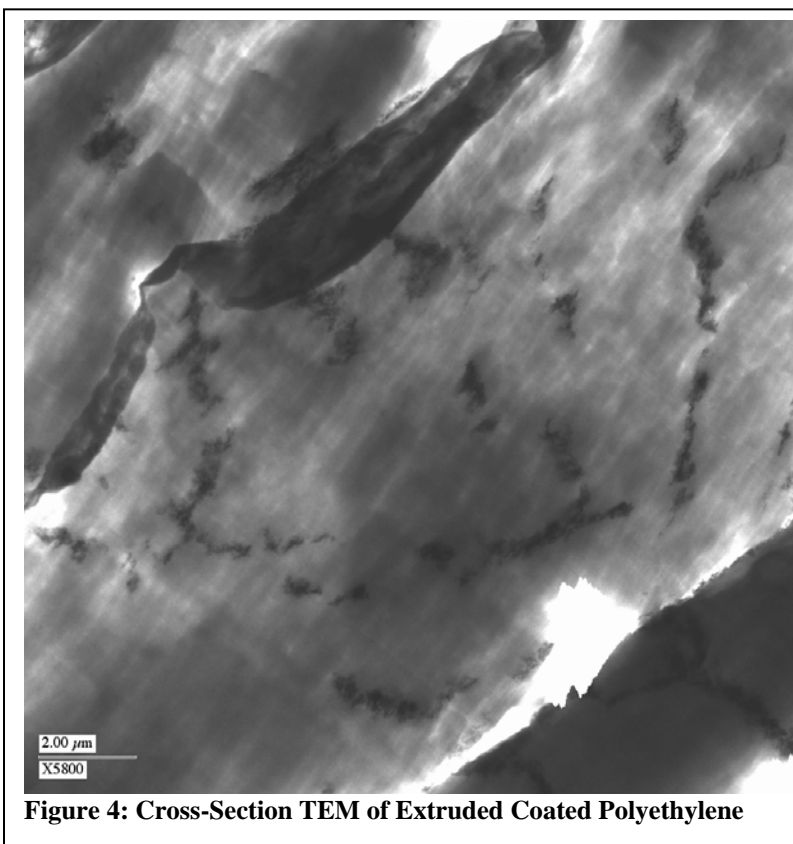
Transmission electron microscopy (TEM) was used to examine extruded polyethylene powder. Samples were cross-sectioned and examined by TEM for dispersed particles.



## Results and Discussion

The ICP-AES data can be compared to previous in situ mass gain observations. Work by C. Wilson, R. Grubbs, and S. George (Unpublished), demonstrated alumina growth on spin coated polyethylene. A quartz crystal microbalance (QCM) was used to monitor mass gain during the experiment. The data from the two techniques can be qualitatively compared to observe similar growth trends as seen in Figure 3.

The beginning lag in growth is due to the aforementioned nucleation of the film. Because polyethylene has no native hydroxyl groups, the fundamental concept of alumina ALD can not take place on the surface. It is believed that nucleation is similar to that of the SiLK polymer in that absorbed reactants combine within the polymer. This can then form small islands and clusters near the surface of the particle. Subsequent



cycles create additional islands and promote growth of established islands until the surface is entirely encapsulated in alumina and only film growth takes place.

Extruded polymer was cross-sectioned and imaged with TEM. Figure 4 is a TEM illustrating dispersed alumina within the HDPE extrusion. The large diagonal features observed in the TEM are small peels in the section resulting from blade chatter of the microtome used for the cross-section. A scattering of nano-sized inclusions of density other than that of the polyethylene substrate can be observed throughout the sample.

## Conclusion

Incorporating an ultra low weight percent of well dispersed material by a novel process has been demonstrated. ALD is used successfully deposit a thin film of alumina onto the surface of individual polyethylene particles. These particles can be extruded normally with the ceramic shells mixing intimately in the mixture. The versatility of atomic layer deposition can also lead to new applications of the same technique with different chemistries, such as incorporating a metal film for a conductive polymer with minimal loading.

---

<sup>i</sup> M. Sumita, H. Tsukihi, K. Miyasaka, and K. Ishikawa, *J. Appl. Polym. Sci.* **29**, 1523 (1984).

<sup>ii</sup> Gilman, J. W.; Jackson, C. L.; Morgan, A. B.; Harris, R.; Manias, E.; Giannelis, E. P.; Wuthenow, M.; Hilton, D.; Philips, S. H. *Chem. Mater.* **2000**, *12*, 1866.

<sup>iii</sup> Linda Schadler, T. M. Apple, B.C. Benicewicz, R.W. Siegel, S.S. Sternstein, B.J. Ash, J. Nugent, D. Rogers, A. Zhu, "Mechanical and Molecular Behavior of Nanoparticle/Polymer Composites", Departments of Materials Science and Engineering and Chemistry, Rensselaer Polytechnic Institute, Troy, NY

<sup>iv</sup> Takami, Y., Nakazawa, T., Makinouchi, K., Glueck, J., Nose, Y., *Journal of Biomedical Materials Research*, **1997**, *36* (3), 381-386

<sup>v</sup> Dillion, A. C.; Ott, A. W.; Way, J. D.; George, S. M. *Surf. Sci.* **1995**, *322*, 230.

<sup>vi</sup> Higashi, G. S.; Fleming, C. G. *Appl. Phys. Lett.* **1989**, *55*, 1963.

<sup>vii</sup> Elam J., Wilson C., Schuisky M., Sechrist Z., George S., *Journal of Vacuum Science and Technology B*, **2003**, *21*, (3), 1099-1107