

Novel Processing to Produce Polymer/Ceramic Nanocomposites by Atomic Layer Deposition

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An innovative process to uniformly incorporate dispersed nanoscale ceramic inclusions within a polymer matrix was demonstrated. Micron-sized high density polyethylene particles were coated with ultrathin alumina films by atomic layer deposition in a fluidized bed reactor at 77°C. The deposition of alumina on the polymer particle surface was confirmed by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. Conformal coatings of alumina were confirmed by transmission electron microscopy and focused ion beam cross-sectional scanning electron microscopy. The results of inductively coupled plasma atomic emission spectroscopy suggested that there was a nucleation period. The results of scanning electron microscopy, particle size distribution, and surface area of the uncoated and nanocoated particles showed that there was no aggregation of particles during the coating process. The coated polymer particles were extruded by a heated extruder at controlled temperatures. The successful dispersion of the crushed alumina shells in the polymer matrix following extrusion was confirmed using cross-sectional transmission electron microscopy. The dispersion of alumina flakes can be controlled by varying the polymer particle size.

I. Introduction

POLYMERIC materials are widely used in packaging applications. Biomedical uses of plastic materials have been widespread and the combination of ceramics and certain polymers is the choice for medical devices.^{1–3} The automobile industry also has embraced plastics to improve efficiency and improve manufacturing methods. However, the strength and some other properties, such as thermal stability, permeability to gases and organic solvents, and flame retardance of the pure polymer

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Work has primarily been done with nanoscopic montmorillonite clay.⁶⁻⁸ Two widely adopted approaches to forming polymer/inorganic nanocomposites are high shear mixing of the preformed polymer with the ceramics (compounding)⁸⁻¹⁰ and *in situ* polymerization of monomer that has been premixed with the ceramics. Both approaches are feasible at the bench scale, but ceramics are not homogeneously dispersed in the polymer matrix at a nanoscopic level⁷ and there are voids between ceramics and polymer. Commercialization will also require a low-cost continuous process. Previous studies show that the combined effects of aspect ratio and dispersion of clay particles ultimately control the mechanical properties of the nanocomposite, with dispersion playing a major role.^{5,6} Relatively few compounding studies have appeared in the literature as a route toward polymer/ceramic nanocomposites.

There is therefore a need to chemically bond ceramics and polymer and disperse ceramics homogeneously throughout the polymer matrix. A novel process to promote intimate mixing is to coat polymer particles with ultrathin, uniform ceramic films. The coated polymer particles can be extruded into pellets or films. During the high shear/high stress extrusion process, the shell on the polymer particle surface will crack and the shell remnants will be dispersed homogeneously throughout the polymer matrix. By means of this novel technique, the mechanical and barrier properties of this kind of polymer/ceramic nanocomposite may be further improved and new advanced features may appear.

There are many problems in depositing inorganic films on polymer surfaces by conventional methods. Chemical vapor deposition (CVD) and plasma-enhanced CVD (PE-CVD) processing have been reported for polymer surface coating.^{11–15} However, typical CVD processes generally operate at temperatures (~300°–500°C) much higher than the softening and melting temperatures of the polymers (~125°–250°C). CVD techniques are not able to effectively control the use of precursor gases or to inherently control the location and the thickness of the ceramic film. In addition, both CVD and PE–CVD will leave defects and pinholes in the deposited inorganic films.^{12–15} Atomic layer deposition (ALD) provides unparalleled advantages over other techniques to deposit inorganic films on polymer surfaces.

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ALD is a surface controlled layer-by-layer process, which deposits low impurity content, pin hole-free, conformal, and ultrathin flexible films.^{16–19} The film thickness is inherently controlled by self-limiting sequential surface chemical reactions, so precursors are used efficiently. ALD has been successfully demonstrated using a fluidized bed reactor (FBR).^{20–23} A FBR has the main advantages of excellent gas/particle contact and thermal efficiency, and its control is easy due to stable operating conditions.

 Al_2O_3 is non-flammable and has a melting point of 2050°C. The chemical and thermal stability of Al_2O_3 allows its application as a good diffusion barrier.²⁴ From a toxicological viewpoint, Al_2O_3 is non-toxic, but the montmorillonite clay can lead to toxic byproducts as the product ages, which may mean that many clay-based nanocomposites will never be suitable for food packaging applications. Therefore, Al_2O_3 is a good alternative to montmorillonite clay. High density polyethylene (HDPE) is a widely used polymer and a good candidate for experimentation. Polyethylene and Al_2O_3 are also biocompatible. Combining these two materials could make a stronger polymer with many potential applications. For example, along with the typical arthroplasty applications for polyethylene, successful biocompatibility has recently been observed for an Al_2O_3 /polyethylene blood pump.³

The main objective of this research is to develop a new costeffective efficient process to fabricate uniform polymer/ceramic nanocomposites. In this paper, the successful deposition of ultra thin Al₂O₃ films on micron-sized HDPE particles by ALD at the temperature of 77° C is reported, and the successful dispersion of Al₂O₃ flakes in the polymer matrix following the extrusion process is demonstrated.

II. Experimental Procedure

 Al_2O_3 films have been deposited on several substrates, using repeated exposures of trimethylaluminum (TMA) and H_2O in an ABAB.....sequence.^{18–23,25–27} Al₂O₃ ALD is derived from the following binary CVD reaction:

$$2\mathrm{Al}(\mathrm{CH}_3)_3 + 3\mathrm{H}_2\mathrm{O} \to \mathrm{Al}_2\mathrm{O}_3 + 6\,\mathrm{CH}_4 \tag{1}$$

This binary reaction can be divided into two half-reactions:

(A) AlOH^{*} + Al(CH₃)₃
$$\rightarrow$$
 [AlOAl(CH₃)₂]^{*} + CH₄ (2)

$$(B) \operatorname{Al}(\operatorname{CH}_3)^* + \operatorname{H}_2 O \to \operatorname{AlOH}^* + \operatorname{CH}_4$$
(3)

where * indicate the surface species.^{17–19} In each half-reaction, a gas-phase precursor reacts with a surface functional group and forms CH₄ as a by-product. The surface reaction continues until all the available surface functional groups have reacted.

The experimental ALD-FBR is shown in Fig. 1. The reactor itself was composed of a 3.5 cm inside diameter stainless steel tube with a 10 μ m pore size porous metal disc as the gas distributor. A 316 L porous metal filter element (1.9 cm ID × 15.24 cm long; 0.5 μ m pore size) was used at the inside top of the reactor column to prevent particles from leaving the system. The reactor was encased by a clamshell-type furnace and bolted to a platform that rested on four large springs. The reactor was maintained at low pressure by a vacuum pump (Model 2063, Alcatel, Paris, France), and the dosing header could also be pumped down directly using a smaller separate pump (Model 2008A, Alcatel). A vibration system (Model



Fig. 1. Schematic diagram of atomic layer deposition–fluidized bed reactor (ALD-FBR): (1) pressure transducers, (2) metal filter, (3) reaction column, (4) distributor plate, (5) vibro-motors, (6) spring supports, (7) pneumatic valves, (8) reactant containers, (9) mass flow controller.

CD36210, Martin Engineering, Marine City, MI) was utilized to overcome some of the interparticle forces and improve the quality of fluidization. High purity N_2 gas was used as the purge gas to remove the unreacted precursor and any CH₄ formed during the reaction. The purge gas flow was fed in through the distributor of the reactor and its flow rate was controlled by a MKS[®] mass flow controller (Model 1179, MKS, Boulder, CO). Piezoelectric transducers (Model 902, MKS) were located below the distributor plate and at the outlet of the reactor column to measure the pressure drop across the bed of the particles. All valves used to provide the transient dosing were automatically controlled through LabView[®] from National Instruments (Austin,TX). Pressure measurements were recorded to monitor the progress of each dosing cycle.

Two different sizes of HDPE particles (Lyondell Chemical, Houston, TX) were used. One had an average size of 16 µm, and the other had an average size of 60 µm. The density of both primary particles was 952 kg/m³. The peak melting point was 134°C. For a typical run, about 20 g of HDPE particles were loaded into the reactor. The feeding lines were kept at about 70°C to avoid excessive absorption of H₂O on the internal walls of the system that could promote CVD reactions. The minimum pressure inside the reactor was about 10 Pa and the minimum fluidization superficial gas velocity was determined by measuring the pressure drop across the bed versus the N₂ superficial gas velocity. Precursors, TMA (Sigma Aldrich, St. Louis, MO) and deionized H₂O, were fed separately through the distributor of the reactor using the driving force of their vapor pressures. The flow rate of TMA and H₂O was adjusted using needle valves to ensure that a precursor pressure was high enough for particle fluidization. The reaction temperature was 77°C, which was lower than the softening/melting point of the HDPE particles. Before the reaction, the particles were dried at 77°C under a continuous N2 flow for 3 h. During each coating cycle, the precursors were fed for enough time so that saturation of all active sites occurred for every dose. A typical coating cycle occurred with the following sequence: dose TMA, purge N₂, evacuate; dose H2O, purge N2, evacuate. In this manner, there is no overlap between the two reactants, and no CVD reactions occur.

A Fourier transform infrared (FTIR) spectrometer (Model 750 Magna-IR, Thermo Nicolet, Waltham, MA) was used to analyze the composition of the HDPE particles before and after coating. The particles were milled with FTIR grade potassium bromide (Sigma Aldrich) to form a very fine powder. This powder was then compressed into a thin pellet using a hydraulic press and polished stainless steel die. An X-ray photoelectron spectroscopy (XPS) system (Model PHI 5600, Physical Electronics, Chanhassen, MN) with a high-energy resolution analyzer was used for this study. Aluminum concentration on HDPE particles was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Model ARL 3410+, Thermo Electron, Waltham, MA). Analysis by ICP-AES was achieved by placing the coated HDPE particles in a strong base solution (NaOH) to dissolve the Al₂O₃ films from the HDPE particles. The HDPE particle itself will not dissolve at normal laboratory conditions. The conformality of the Al₂O₃ coatings on the HDPE particles was evaluated by transmission electron microscope (TEM; Model CM 10, Philips, Eindhoven, the Netherlands). The morphology of the HDPE particles before and after coating was investigated by scanning electron microscope (SEM; Model JSM-6400, JEOL, Tokyo, Japan). The size distribution of HDPE particles was performed using an Aerosizer particle size analyzer (Model 3225, TSI, Shoreview, MN). Surface area analysis was performed using a physisorption analyzer (Model Autosorb¹⁰-1, Quantachrome, Boynton Beach, FL).

The coated particles were extruded by a bench-sized, heated extruder (Bonnot, Uniontown, OH) at controlled temperatures. 16 and 60 μ m HDPE particles were extruded at 135° and 175°C, respectively. To extrude a ribbon of polymer, the ribbon die was attached downstream of the heated barrel of the extruder. HDPE/Al₂O₃ nanocomposite films comprising various levels

of concentration and morphologies of nanoscale ceramic flakes were formed. The structure information of the nanocomposite films was confirmed by cross-sectional TEM.

III. Results and Discussion

(1) Test for Composition of Al_2O_3 Films on HDPE Particles The composition of HDPE particles (16 um) before and often

The composition of HDPE particles (16 µm) before and after coating was characterized by *ex situ* FTIR spectroscopy. As shown in Fig. 2, the FTIR spectrum of the reference alumina sample shows the Al_2O_3 bulk vibrational mode at the frequency of 1100–500 cm⁻¹ and the vibration of the OH group at the frequency of 3700–3000 cm^{-1.25} No above-mentioned Al_2O_3 and OH group features are observed for uncoated HDPE particles. An Al_2O_3 vibrational mode and a broad OH group feature appear for coated particles after 25 and 50 cycles. This is a direct confirmation of the composition of the Al_2O_3 films on the polymer surface. For HDPE samples, the features at 3000–2800, 1460, and 720 cm⁻¹ are attributed to C–H stretching, deformation, and rocking modes of CH₂ groups.²⁵

XPS measurements were also performed on uncoated and Al₂O₃ coated HDPE particles (16 µm) after 50 cycles. The analysis was performed using an aluminum source, pass energy of 187.85 eV, and an energy step of 0.2 eV. In Fig. 3, the spectrum for the uncoated HDPE particles shows a photoelectron peak at 284.7 eV (C, 1s). In contrast, the carbon spectrum for coated HDPE particles reveals much weaker photoelectron intensity at 284.7 eV. This reduction of carbon signal is expected if the Al₂O₃ film conformally covers the entire polymer particle. The carbon XPS signal cannot be completely attenuated as some of it corresponds to surface carbon. Photoelectrons from the Al₂O₃-coated HDPE particles are observed at 118.7 eV (Al. 2s), 73.9 eV (Al, 2p) and 530.7 eV (O, 1s). It is clearly evident that there is only a single peak centered at 73.9 eV, which corresponds to Al-O bonds of Al₂O₃. The absence of a shoulder region around 72.5 eV, which corresponds to Al-Al bonds, clearly confirms that the aluminum metal is not present in our films.^{28,29} So, the XPS results corroborate the FTIR results and verify the composition of deposited Al₂O₃ films on the HDPE particles.

(2) Uniformity of Al_2O_3 Films on HDPE Particles

In order to study the uniformity of Al_2O_3 films on HDPE particles, TEM analysis was performed at 100 kV on the coated particles (16 µm) after 50 cycles. The TEM image in Fig. 4 shows that an Al_2O_3 film was successfully coated on the particle surface. The contrast between the film and the particle substrate is given by the difference in density between Al_2O_3 and HDPE. The thickness of the Al_2O_3 films is about 23 ± 4 nm, which



Fig. 2. Fourier transform infrared spectra of uncoated high density polyethylene particles, Al₂O₃-coated HDPE particles, and reference Al₂O₃ powders.



Fig. 3. X-ray photoelectron spectroscopy spectra of (a) uncoated and (b) Al_2O_3 -coated high density polyethylene particles (16 μ m) after 50 cycles.

represents a growth rate of about 0.5 nm per coating cycle at this experimental condition. The Al_2O_3 films appear to be very uniform and smooth.

Focused ion beam (FIB) cross-sectional SEM imaging allows precise observation at the edge interface of the polymer and Al₂O₃ film. The FIB cross-sectional SEM image of HDPE particles (60 μ m) after 100 cycles is shown in Fig. 5. Al₂O₃ islands began to grow below the polymer surface and the film merged into a linear layer as it grew. Approximately 35±7 nm thick Al₂O₃ films were coated on the polymer surface. This thickness represents a growth rate of about 0.4 nm per coating cycle at this experimental condition. The SEM image also shows that the Al₂O₃ films appear to be very uniform and smooth.

The Al₂O₃ film growth rate was much higher than the 0.11–0.13 nm per cycle of an ALD process reported in the literature.¹⁹ Recent FTIR measurements of Al₂O₃ ALD on low density polyethylene (LDPE) indicated the presence of hydrogen-bonded H₂O molecules on the Al₂O₃ surface.²⁵ This higher growth rate may be explained by the presence of hydrogen-bonded H₂O. This H₂O can react with TMA to deposit additional Al₂O₃ by CVD.²⁵ Another reason is the increase in the surface coverage of reactants at lower temperatures.^{30,31} Though the reaction kinetics is slower at lower temperatures, the growth rate is determined by the higher surface coverage.^{30,31} Also, it is important to mention that the growth rate of films may vary with the size and geometry of the substrate.²² For particles with a high ratio of curvature, more active sites on the surface are exposed to the gas phase reactants. The different initial surfaces may partly explain the discrepancy between Al₂O₃ growth rates on the HDPE particles and on some other substrates.



Fig. 5. Focused ion beam cross-sectional scanning electron micrograph of Al_2O_3 -coated high density polyethylene (HDPE) particle (60 μ m) after 100 cycles.

(3) Nucleation and Linear Growth of Al_2O_3 Films After Nucleation

The concentration of aluminum on HDPE particles was analyzed by ICP-AES. ICP-AES provides the concentration in parts per million (ppm) by mass of aluminum in relation to the HDPE particles. The ICP-AES aluminum concentration versus number of coating cycles is shown in Fig. 6. The average diameter of the particles was 16 μ m. The lower growth rate of Al₂O₃ before 25 cycles shows that there is a delay before film growth starts, which verifies that a nucleation period is needed for the deposition of Al₂O₃ on an HDPE particle surface.³² From this plot, the nucleation period is 10 cycles at this experimental condition.

The Al₂O₃ ALD is conventionally thought to begin with native hydroxyl groups on the surface. HDPE, however, is one kind of saturated hydrocarbon, which lacks typical chemical functional groups such as hydroxyl species that are necessary to initiate the growth of an inorganic film. So, the fundamental concept of Al₂O₃ ALD cannot take place on the HDPE particle surface. The nucleation of Al₂O₃ ALD on HDPE requires a mechanism that does not involve the direct reaction between TMA and HDPE. Consequently, an alternative mechanism is needed to explain the Al₂O₃ ALD on HDPE.

HDPE has a porous surface, which is due to the interstitial space between individual molecules as HDPE does not have the regular lattice-type structure found in metals. Both HDPE and TMA are nonpolar, so it is expected that TMA has a reasonable solubility in the HDPE particles, and TMA can adsorb onto the surface of the polymer and subsequently diffuse into the near-surface regions of the polymer.^{25,32} During the ALD reaction,



Fig. 4. Transmission electron micrograph of Al_2O_3 -coated high density polyethylene particle (16 μ m) after 50 cycles.



Fig. 6. Aluminum concentration on high density polyethylene particles versus coating cycles.

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TMA will be first exposed to the HDPE particles and diffuse into the bulk of the polymer matrix; therefore, the incoming H₂O will react efficiently with TMA molecules at or near the surface of the polymer particles and Al₂O₃ clusters will be formed. The pores on the particle surface will become smaller and will gradually close with progressive coating cycles. After several coating cycles, the Al₂O₃ clusters will eventually merge to create a continuous adhesion layer on the polymer particle surface. This phenomenon can be observed in Fig. 5. Al₂O₃ clusters with hydroxyl groups will provide a "foothold" for the deposition of Al₂O₃ films on the polymer. As shown in Fig. 6, the concentration of aluminum is almost directly proportional to the number of coating cycles after 25 cycles, which indicates a constant growth rate and a linear dependence between the film thickness and number of growth cycles after a nucleation period. The model of the predicted growth mechanism is illustrated in Fig. 7.

(4) Effect of Coating on Particle Size Distribution and Surface Area

Fine particles will aggregate during fluidization because of interparticle forces, such as Van der Waals forces.²⁰ SEM was used to analyze the morphology of the HDPE particles (16 μ m) before and after coating. SEM analysis was performed at 15 kV. Figure 8 shows that no aggregates were coated; rather, particles were coated individually.

This is also confirmed by the results of particle size distribution (PSD) of HDPE particles (16 μ m) before and after coating. The PSD curves for uncoated particles and Al₂O₃-coated particles after 50 cycles are shown in Fig. 9. As shown in the plot, the size of particles remains fairly unchanged after the coating process, meaning that no aggregates were being coated. If aggregates of particles were coated and glued together, the size distribution of particles after coating would drastically shift to the right.

In addition to PSD analysis, Brunauer–Emmett–Teller (BET) measurements indicated that the surface area of Al_2O_3 coated HDPE particles (16 µm) after 50 cycles was $0.72 \pm 0.02 \text{ m}^2/\text{g}$, which was very close to that of uncoated HDPE particles ($0.70 \pm 0.03 \text{ m}^2/\text{g}$). A drastic decrease in surface area, which did not occur, would have indicated necking of particles.²⁰ This result also indicated that the individual particles were coated as opposed to necking multiple particles together in the FBR.

(5) Structure Information of Nanocomposite Films

The $16 \ \mu m \ Al_2O_3$ -coated HDPE particles after 75 cycles and the 60 $\ \mu m \ Al_2O_3$ -coated HDPE particles after 100 cycles were extruded to crush Al_2O_3 shell coatings. Remnants of the crushed shell coatings were then dispersed throughout the polymer. The extruded nanocomposite films were cut using a microtome to achieve a thickness of approximately 100 nm for TEM analysis. The cross-sectional TEM images of the nanocomposite films are shown in Fig. 10. These two images show a scattering of nano-



Fig. 7. Proposed Al_2O_3 growth mechanism.





Fig.8. Scanning electron microscopy of (a) uncoated and (b) Al_2O_3 -coated high density polyethylene particles (16 μ m) after 75 cycles.

sized inclusions of Al₂O₃ throughout the samples. The brightest spots are areas in the films where the rough microtoming penetrated the films. In Fig. 10(a), the smaller image on the top left corner represents one of the Al₂O₃ flakes at higher magnification, which indicates that Al₂O₃ flakes were formed of much smaller Al₂O₃ particles. The desired loading percent of Al₂O₃ can be controlled by adjusting starting polymer particle size. In the case of HDPE particles with the size of 16 µm, as shown in Fig. 10(b), more Al₂O₃ flakes were dispersed in the matrix, and the Al₂O₃ flakes were dispersed more homogeneously. Hence, the dispersion of Al₂O₃ flakes can be controlled by varying the polymer particle size.

IV. Conclusions

This work represents the first successful attempt to fabricate polymer/ceramic nanocomposites by extruding nanocoated



Fig. 9. Particle size distribution of uncoated and Al_2O_3 -coated high density polyethylene particles (16 μ m) after 50 cycles.

References

¹M. A. Araújo, C. M. Vaz, A. M. Cunha, and M. Mota, "In-Vitro Degradation Behaviour of Starch/EVOH Biomaterials," Polym. Degrad. Stabil., 73 [2] 237-44 (2001)

²H. Warashina, S. Sakano, S. Kitamura, K.-I. Yamauchi, J. Yamaguchi, N. Ishiguro, and Y. Hasegawa, "Biological Reaction to Alumina, Zirconia, Titanium, and Polyethylene Particles Implanted onto Murine Calvaria," Biomaterials, 24 [21] 3655-61 (2003).

³Y. Takami, T. Nakazawa, K. Makinouchi, J. Glueck, and Y. Nose, "Biocompatibility of Alumina Ceramic and Polyethylene as Materials for Pivot Bearings of a Centrifugal Blood Pump," J. Biomed. Mater. Res., 36 [3] 381-6 (1997).

⁴J. H. Yeo, C. H. Lee, C.-S. Park, K.-J. Lee, J.-D. Nam, and S. W. Kim, "Rheological, Morphological, Mechanical, and Barrier Properties of PP/EVOH Blends," Adv. Polym. Technol., 20 [3] 191–201 (2001).

⁵P. Maiti, K. Yamada, M. Okamoto, K. Ueda, and K. Okamoto, "New Polylactide/Layered Silicate Nanocomposites: Role of Organoclays," Chem. Mater, 14

⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, ⁶A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, Y. and O. Kamigaito, "Synthesis of Nylon 6-Clay Hybrid," J. Mater. Res., 8 [5] 1179-84 (1993).

⁷Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi, O. Kamigaito, and K. Kaji, "Fine-Structure of Nylon-6-Clay Hybrid," J. Polym. Sci. Pt. B-Polym. Phys., 32 [4] 625-30 (1994).

⁸P. B. Messersmith and E. P. Giannelis, "Synthesis and Barrier Properties of Poly(epsilon-Caprolactone)-Layered Silicate Nanocomposites," J. Polym. Sci. Pol. Chem., 33 [7] 1047-57 (1995).

⁹J. W. Gilman, L. Jackson, A. B. Morgan, R. Harris, E. Manias, E. P. Giannelis, M. Wuthenow, D. Hilton, and S. H. Phillips, "Flammability Properties of Polymer-Layered-Silicate Nanocomposites. Polypropylene and Polystyrene Nanocomposites," Chem. Mater, 12 [7] 1866-73 (2000).

¹⁰E. L. Cussler, S. E. Hughes, W. J. Ward, and R. Aris, "Barrier Membranes," J. Membr. Sci., 38 [2] 161–74 (1988).

¹¹F. Breme, J. Buttstaedt, and G. Emig, "Coating of Polymers with Titanium-Based Layers by a Novel Plasma-Assisted Chemical Vapor Deposition Process,' Thin Solid Films, 377, 755-9 (2000).

¹²A. P. Roberts, B. M. Henry, A. P. Sutton, C. R. M. Grovenor, G. A. D. Briggs, T. Miyamoto, M. Kano, Y. Tsukahara, and M. Yanaka, "Gas Permeation in Silicon-Oxide/Polymer (SiOx/PET) Barrier Films: Role of the Oxide Lattice, Nano-Defects, and Macro-Defects," J. Membr. Sci., 208 [1-2] 75-88 (2002). ¹³A. S. D. Sobrinho, G. Czeremuszkin, M. Latrèche, G. Dennler, and M. R.

Wertheimer, "A Study of Defects in Ultra-Thin Transparent Coatings on Poly-¹⁴A. S. D. Sobrinho, G. Czeremuszkin, M. Latrèche, and M. R. Wertheimer,

"Defect-Permeation Correlation for Ultrathin Transparent Barrier Coatings on Polymers," J. Vac. Sci. Technol., A, 18 [1] 149-57 (2000).

G. L. Graff, R. E. Williford, and P. E. Burrows, "Mechanisms of Vapor Permeation Through Multilayer Barrier Films: Lag Time Versus Equilibrium Permeation," *J. Appl. Phys.*, **96** [4] 1840–9 (2004). ¹⁶T. Suntola, "Atomic Layer Epitaxy," *Thin Solid Films*, **216** [1] 84–9

(1992)

¹⁷S. M. George, A. W. Ott, and J. W. Klaus, "Surface Chemistry for Atomic Layer Growth," *J. Phys. Chem.*, **100** [31] 13121–31 (1996).

A. C. Dillon, A. W. Ott, J. D. Way, and S. M. George, "Surface Chemistry of Al2O3 Deposition Using Al(CH3)3 and H2O in a Binary Reaction Sequence," Surf. Sci., **322** [1–3] 230-42 (1995). ¹⁹A. W. Ott, J. W. Klaus, J. M. Johnson, and S. M. George, "Al₂O₃ Thin Film

Growth on Si(100) Using Binary Reaction Sequence Chemistry," Thin Solid Films, ²⁰J. R. Wank, S. M. George, and A. W. Weimer, "Nanocoating Individual

Cohesive Boron Nitride Particles in a Fluidized Bed by ALD," Powder Technol., **142** [1] 59–69 (2004). ²¹J. R. Wank, S. M. George, and A. W. Weimer, "Coating Fine Nickel Particles

with Al2O3 Utilizing an Atomic Layer Deposition-Fluidized Bed Reactor (ALD-FBR)," J. Am. Ceram. Soc., 87 [4] 762-5 (2004).

²L. F. Hakim, S. M. George, and A. W. Weimer, "Conformal Nanocoating of Zirconia Nanoparticles by Atomic Layer Deposition in a Fluidized Bed Reactor, Nanotechnology, 16 [7] \$375-81 (2005).

²³L. F. Hakim, J. Blackson, S. M. George, and A. W. Weimer, "Nanocoating Individual Silica Nanoparticles by Atomic Layer Deposition in a Fluidized Bed Reactor," Chem. Vapor Depos., 11 [10] 420-5 (2005).

⁴G. D. Wilk, R. M. Wallace, and J. M. Anthony, "High-kappa Gate Dielectrics: Current Status and Materials Properties Considerations," J. Appl. Phys., 89 [10] 5243–75 (2001).
²⁵J. D. Ferguson, A. W. Weimer, and S. M. George, "Atomic Layer

Deposition of Al₂O₃ Films on Polyethylene Particles," Chem. Mater., 16 [26] 5602-9 (2004).
²⁶N. Kawakami, Y. Yokota, T. Tachibana, K. Hayashi, and K. Kobashi,

"Atomic Layer Deposition of Al2O3 Thin Films on Diamond," Diam. Relat. Mater., 14 [11-12] 2015-8 (2005).

A. Paranjpe, S. Gopinath, T. Omstead, and R. Bubber, "Atomic Layer Deposition of AlOx for Thin Film Head Gap Applications," J. Electrochem. Soc., 148 ^[9] G465–71 (2001). ²⁸Y.-C. Jung, H. Miura, K. Ohtani, and M. Ishida, "High-Quality Silicon/In-

sulator Heteroepitaxial Structures Formed by Molecular Beam Epitaxy Using Al₂O₃ and Si," J. Cryst. Growth, 196 [1] 88-96 (1999).

²⁵W. S. Yang, Y. K. Kim, S.-Y. Yang, J. H. Choi, H. S. Park, S. I. Lee, and J.-B. Yoo, "Effect of SiO₂ Intermediate Layer on Al₂O₃/SiO₂/n⁺-Poly

Fig. 10. Cross-sectional transmission electron micrograph of (a) high density polyethylene/Al₂O₃ nanocomposite extruded from 60 µm Al₂O₃coated HDPE particles after 100 cycles and (b) HDPE/Al₂O₃ nanocomposite extruded from 16 µm Al₂O₃-coated HDPE particles after 75 cycles.

polymer particles. Micron-sized HDPE particles were coated with an ultrathin Al₂O₃ film in a fluidized bed reactor by atomic layer deposition at a large scale. The FTIR and XPS revealed that Al₂O₃ films were deposited on the polymer particle surface. TEM and FIB cross-sectional SEM revealed ultrathin and conformal Al₂O₃ coatings. A nucleation mechanism for Al₂O₃ atomic layer deposition on the polymer surface was confirmed. The results of ICP-AES suggested a nucleation period of 10 coating cycles, after which, a linear dependence between the film thickness and number of growth cycles was verified. The results of SEM, particle size distribution, and surface area of the uncoated and nanocoated particles showed that the particles were not coated as agglomerates during the coating process, rather as individual particles.

Al₂O₃-coated HDPE particles were successfully extruded into HDPE/Al₂O₃ nanocomposite films by a heated extruder at controlled temperatures. Cross-sectional TEM indicated that nanoscale Al₂O₃ flakes were successfully dispersed in the polymer matrix. The dispersion of Al₂O₃ flakes can be controlled by varying the polymer particle size. The process, firmly depositing nearly perfect nanometer thick ceramic films on polymer particle surfaces by atomic layer deposition and then extruding the coated polymer particles into final products, will provide unparalleled opportunities to produce quality nanocomposites with improved mechanical properties and reduced permeability in a continuous high throughput process at low cost.

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Si Interface Deposited Using Atomic Layer Deposition (ALD) for Deep Submicron Device Applications," *Surf. Coat. Technol.*, **131** [1–3] 79–83 (2000).

(2000).
³⁰M. D. Groner, F. H. Fabreguette, J. W. Elam, and S. M. George, "Low-Temperature Al₂O₃ Atomic Layer Deposition," *Chem. Mater.*, **16** [4] 639–45 (2004).

³¹J. W. Klaus, O. Sneh, and S. M. George, "Growth of SiO₂ at Room Temperature with the Use of Catalyzed Sequential Half–Reactions," *Science*, **278** [5345] 1934–6 (1997).

[5345] 1934-6 (1997). ³²C. A. Wilson, R. K. Grubbs, and S. M. George, "Nucleation and Growth During Al₂O₃ Atomic Layer Deposition on Polymers," *Chem. Mater.*, **17** [23] 5625–34 (2005).