

Conductive Thin Films on Functionalized Polyethylene Particles

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Hyperbranched polyethylenimine (PEI) is covalently grafted to the surface of polyethylene (PE) particles in an effort to promote the growth of conductive thin films deposited using layer-by-layer (LbL) assembly. Growth of the grafting process is monitored with infrared spectroscopy and titration. LbL films are then deposited using dilute aqueous mixtures containing carbon black stabilized with PEI or poly(acrylic acid). Deposition of carbon black-filled bilayers on PEI-grafted PE shows uniform surface coverage and strong bonding after just two bilayers, while neat PE shows patchy film growth and poor adhesion, requiring eight bilayers to achieve full surface coverage. Acid-oxidized PE shows intermediate behavior with regard to deposition but shows weak bonding like neat PE. LbL films are characterized using electron microscopy and thermogravimetric analysis, which show linear growth for PEI-grafted particles and nonlinear growth for neat and acid-oxidized particles. Following carbon black deposition, the electrical conductivities of films made by compressing the coated particles were compared. No conductivity can be measured for films made with neat PE particles containing two and four bilayers, but acid-oxidized and PEI-grafted systems exhibit conductivities of 0.000 004 5 and 0.01 S/cm, respectively. Plotting conductivity as a function of carbon black concentration reveals a percolation threshold below 0.01 wt % and a conductivity of 0.2 S/cm with just 6 wt %. This combination of covalent polyelectrolyte grafting and LbL deposition could potentially be used to impart useful properties to a variety of polyolefin surfaces.

1. Introduction

Layer-by-layer (LbL) assembly, formerly called electrostatic self-assembly, is a method used to impart functionality to the surface of nearly any type of substrate.^{1,2} Thin films are deposited by alternately exposing a substrate to aqueous mixtures (or solutions) of mutually attractive molecules or particles. In most cases the attraction between species is provided by charge and each combination of a positively and negatively charged layer is referred to as a “bilayer”. Each deposited layer is typically 1–100 nm thick depending on charge density,^{3,4} counterion,³ molecular weight,⁵ temperature,⁶ deposition time,^{7,8} and pH^{9,10} of the species being deposited. Concentration⁸ and ionic strength^{8,11} of the deposition mixture will also influence layer thickness. LbL-based

thin films can impart chemical sensing,^{12–14} electrically conductive,^{15,16} super-hydrophobic,¹⁷ electrochromic,^{18,19} magnetic,²⁰ and antimicrobial behavior^{21,22} to a given substrate. While substrates for LbL assembly are usually flat surfaces, there is no shape limitation, and a variety of studies have demonstrated the ability to uniformly coat small spherical particles.^{23–26} In most cases these thin coatings are used for some form of encapsulation rather than providing an active functionality. In the present study polyethylenimine (PEI) was grafted to the surface of irregularly shaped polyethylene

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- (1) Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. *Macromol. Rapid Commun.* **2000**, *21*, 319–348.
- (2) Decher, G.; Schlenoff, J. B. *Multilayer Thin Films-Sequential Assembly of Nanocomposite Materials*; Wiley-VCH: Weinheim, Germany, 2003.
- (3) Mermut, O.; Barrett, C. J. *J. Phys. Chem. B* **2003**, *107*, 2525–2530.
- (4) Schoeler, B.; Poptoshev, E.; Caruso, F. *Macromolecules* **2003**, *36*, 5258–5264.
- (5) Sui, Z. J.; Salloum, D.; Schlenoff, J. B. *Langmuir* **2003**, *19*, 2491–2495.
- (6) Tan, H. L.; McMurdo, M. J.; Pan, G. Q.; Van Patten, P. G. *Langmuir* **2003**, *19*, 9311–9314.
- (7) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **1999**, *32*, 8153–8160.
- (8) Zhang, H. N.; Ruhe, J. *Macromolecules* **2003**, *36*, 6593–6598.
- (9) Shiratori, S. S.; Rubner, M. F. *Macromolecules* **2000**, *33*, 4213–4219.
- (10) Choi, J.; Rubner, M. F. *Macromolecules* **2005**, *38*, 116–124.
- (11) McAloney, R. A.; Sinyor, M.; Dudnik, V.; Goh, M. C. *Langmuir* **2001**, *17*, 6655–6663.

- (12) Lee, S. H.; Kumar, J.; Tripathy, S. K. *Langmuir* **2000**, *16*, 10482–10489.
- (13) Tian, S. J.; Liu, J. Y.; Zhu, T.; Knoll, W. *Chem. Mater.* **2004**, *16*, 4103–4108.
- (14) Jiang, C. Y.; Markutsya, S.; Pikus, Y.; Tsukruk, V. V. *Nat. Mater.* **2004**, *3*, 721–728.
- (15) Zhang, F. X.; Srinivasan, M. P. *Thin Solid Films* **2005**, *479*, 95–102.
- (16) Jan, C. J.; Walton, M. D.; McConnell, E. P.; Jang, W.-S.; Kim, Y. S.; Grunlan, J. C. *Carbon* **2006**, in press.
- (17) Jisr, R. M.; Rmaile, H. H.; Schlenoff, J. B. *Angew. Chem., Int. Ed.* **2005**, *44*, 782–785.
- (18) DeLongchamp, D. M.; Kastantin, M.; Hammond, P. T. *Chem. Mater.* **2003**, *15*, 1575–1586.
- (19) Liu, S. Q.; Kurth, D. G.; Mohwald, H.; Volkmer, D. *Adv. Mater.* **2002**, *14*, 225 ff.
- (20) Mamedov, A. A.; Kotov, N. A. *Langmuir* **2000**, *16*, 5530–5533.
- (21) Boulmedais, F.; Frisch, B.; Etienne, O.; Laval, P.; Picart, C.; Ogier, J.; Voegel, J. C.; Schaaf, P.; Egles, C. *Biomaterials* **2004**, *25*, 2003–2011.
- (22) Grunlan, J. C.; Choi, J. K.; Lin, A. *Biomacromolecules* **2005**, *6*, 1149–1153.
- (23) Schuetz, P.; Caruso, F. *Adv. Funct. Mater.* **2003**, *13*, 929–937.
- (24) Lvov, Y. M.; Price, Y. R. *Colloids Surf., B* **2002**, *23*, 251–256.
- (25) Sukhishvili, S. A. *Curr. Opin. Colloid Interface Sci.* **2005**, *10*, 37–44.
- (26) Correa-Duarte, M. A.; Kosiorek, A.; Kandulski, W.; Giersig, M.; Liz-Marzan, L. M. *Chem. Mater.* **2005**, *17*, 3268–3272.

(PE) particles in an effort to promote stable growth of carbon black (CB) thin films.

Many materials can be used as a substrate for LbL deposition without the need for surface modification, but there is difficulty building layers on polyolefins.^{27,28} It is difficult to get water-based coatings to adhere well to polyolefins, such as PE and polypropylene, because of low surface energy and lack of polarity. Corona or plasma treatments can be used to increase the surface energy of polyolefin films.^{29–32} Both of these techniques generate polar functionalities on the film surface that will improve wetting and subsequent adhesion of an aqueous coating. Oxidative acid etching is another method that generates hydroxyl and carboxylic acid species to create surface polarity.³³ However, these surface modification techniques only produce monolayers of functionality whose properties change upon surface reorganization. A more recent technique, used here to promote stable LbL film growth and stronger adhesion, is the growth or graft of polyelectrolytes on polyolefin.^{34–37} In the present study, a hyperbranched PEI surface was generated on PE particles in a manner similar to that done previously on a silica support.³⁷ Hyperbranching yields a uniform surface coverage of polyelectrolyte down to the microscopic level, despite initial growth occurring only sparsely over the PE particle surface. The presence of PEI on the PE particle then facilitates near perfect surface coverage by alternate deposition of CB stabilized with poly(acrylic acid) (PAA) and PEI in a LbL fashion. Untreated PE exhibits very poor acceptance of the LbL film growth under the same conditions, while oxidative acid etching exhibits intermediate behavior. The CB-coated particles so formed produce highly conductive composites when compression molded.

CB-filled polymer composites are useful as thermal resistors,^{38,39} chemical sensors,^{40,41} electromagnetic interference shielding,^{42,43} and electrostatic dissipation layers.^{43,44} Such electrically conductive composites are typically prepared using melt mixing^{45,46} or solution processing.^{47,48} These

methods lead to composites with high percolation thresholds because of random CB dispersion. The percolation threshold is the minimum concentration of conductive filler required to generate a conductive pathway that travels through the entire composite film.⁴⁹ In many cases, the high CB concentrations (>25 wt %) required to achieve significant electrical conductivity is often accompanied by high mixing viscosity and brittle composite films with extensive porosity due to aggregated filler.^{50,51} LbL deposition circumvents high viscosity processing by using dilute mixtures (<1 wt % solids) to deposit layers of CB that are pre-stabilized with PEI and PAA to impart basic and acidic surface chemistry, respectively. The resulting films are thin (<1 μm), flexible, and dense, with a high concentration of CB (>45 wt %).¹⁶ When applied to PEI-treated PE particles, with an average particle size of 1.7 μm , highly conductive composites are produced that have a very small weight fraction of CB following compaction. Unlike typical composites formed with a random dispersion of CB, a segregated network is generated as the thin conductive shells are pressed together, leading to high conductivity even at very low CB concentration. The segregated network concept relies on a polymer matrix with an exclusionary microstructure.⁵² In essence, the conductive filler is given a restricted volume in which to reside that leads to network formation at very low concentration. Larger polymer particles or domain size relative to the conductive particle size yields lower percolation thresholds.⁵³ A variety of segregated network composites have been produced using polymer blends,^{54–58} powders,^{53,59,60} and emulsions^{61,62} to produce excluded volume during processing. The composites made with CB typically have percolation thresholds from 1.5 to 7.5 wt % and maximum electrical conductivity (plateau of conductivity as a function of CB concentration) from 0.01 to 1 S/cm, with lower percolation thresholds accompanied by reduced maximum conductivity.^{54–58,60,61}

In this work, a comparison is made between the untreated PE particle, the oxidative acid etched particle, and the particle that has hyperbranched PEI on its surface. Infrared spec-

- (27) Delcorte, A.; Bertrand, P.; Wischerhoff, E.; Laschewsky, A. *Langmuir* **1997**, *13*, 5125–5136.
- (28) Greene, G.; Tannenbaum, R. *Appl. Surf. Sci.* **2004**, *233*, 336–342.
- (29) Hougen, L. R. *Nature* **1960**, *188*, 577–578.
- (30) Carley, J. F.; Kitz, P. T. *Polym. Eng. Sci.* **1978**, *18*, 326–334.
- (31) Morra, M.; Occhiello, E.; Gila, L.; Garbassi, F. *J. Adhes.* **1990**, *33*, 77–88.
- (32) Nihlstrand, A.; Hjertberg, T.; Johansson, K. *Polymer* **1997**, *38*, 3581–3589.
- (33) Blais, P.; Carlsson, D. J.; Csullog, G. W.; Wiles, D. M. *J. Colloid Interface Sci.* **1974**, *47*, 636–649.
- (34) Bergbreiter, D. E. *Prog. Polym. Sci.* **1994**, *19*, 529–560.
- (35) Tao, G. L.; Gong, A. J.; Lu, J. J.; Sue, H. J.; Bergbreiter, D. E. *Macromolecules* **2001**, *34*, 7672–7679.
- (36) Bergbreiter, D. E.; Boren, D.; Kippenberger, A. M. *Macromolecules* **2004**, *37*, 8686–8691.
- (37) Bergbreiter, D. E.; Simanek, E. E.; Owsik, I. J. *Polym. Sci., Polym. Chem.* **2005**, *43*, 4654–4665.
- (38) Brodeur, S. A.; Huebner, W.; Runt, J. P.; Newnham, R. E. *J. Mater. Res.* **1991**, *6*, 175–182.
- (39) Wan, Y.; Wen, D. J. *Smart Mater. Struct.* **2004**, *13*, 983–989.
- (40) Kim, Y. S.; Ha, S. C.; Yang, Y.; Kim, Y. J.; Cho, S. M.; Yang, H.; Kim, Y. T. *Sens. Actuators, B* **2005**, *108*, 285–291.
- (41) Koscho, M. E.; Grubbs, R. H.; Lewis, N. S. *Anal. Chem.* **2002**, *74*, 1307–1315.
- (42) Das, N. C.; Chaki, T. K.; Khastgir, D.; Chakraborty, A. *Adv. Polym. Technol.* **2001**, *20*, 226–236.
- (43) Klason, C.; McQueen, D. H.; Kubat, J. *Macromol. Symp.* **1996**, *108*, 247–260.
- (44) Kale, V.; Moukwa, M. *J. Electrostat.* **1996**, *38*, 239–248.

- (45) Lee, G. J.; Suh, K. D.; Im, S. S. *Polym. Eng. Sci.* **1998**, *38*, 471–477.
- (46) Feller, J. F.; Linossier, I.; Levesque, G. *Polym. Adv. Technol.* **2002**, *13*, 714–724.
- (47) Tang, H.; Chen, X. F.; Luo, Y. X. *Eur. Polym. J.* **1996**, *32*, 963–966.
- (48) Schueler, R.; Petermann, J.; Schulte, K.; Wentzel, H. P. *J. Appl. Polym. Sci.* **1997**, *63*, 1741–1746.
- (49) Kirkpatrick, S. *Rev. Mod. Phys.* **1973**, *45*, 574–588.
- (50) Grunlan, J. C.; Gerberich, W. W.; Francis, L. F. *J. Mater. Res.* **1999**, *14*, 4132–4135.
- (51) Souza, F. G.; Sena, M. E.; Soares, B. G. *J. Appl. Polym. Sci.* **2004**, *93*, 1631–1637.
- (52) Kusy, R. P. *J. Appl. Phys.* **1977**, *48*, 5301–5305.
- (53) Malliaris, A.; Turner, D. T. *J. Appl. Phys.* **1971**, *42*, 614–618.
- (54) Thongruang, W.; Balik, C. M.; Spontak, R. J. *J. Polym. Sci., Polym. Phys.* **2002**, *40*, 1013–1025.
- (55) Sumita, M.; Sakata, K.; Hayakawa, Y.; Asai, S.; Miyasaka, K.; Tanemura, M. *Colloid Polym. Sci.* **1992**, *270*, 134–139.
- (56) Breuer, O.; Tchoudakov, R.; Narkis, M.; Siegmann, A. *J. Appl. Polym. Sci.* **1997**, *64*, 1097–1106.
- (57) Feng, J. Y.; Chan, C. M.; Li, J. X. *Polym. Eng. Sci.* **2003**, *43*, 1058–1063.
- (58) Foulger, S. H. *J. Polym. Sci., Polym. Phys.* **1999**, *37*, 1899–1910.
- (59) Bouchet, J.; Carrot, C.; Guillet, J.; Boiteux, G.; Seytre, G.; Pineri, M. *Polym. Eng. Sci.* **2000**, *40*, 36–45.
- (60) Yacubowicz, J.; Narkis, M.; Benguigui, L. *Polym. Eng. Sci.* **1990**, *30*, 459–468.
- (61) Grunlan, J. C.; Gerberich, W. W.; Francis, L. F. *J. Appl. Polym. Sci.* **2001**, *80*, 692–705.
- (62) Wang, Y. C.; Anderson, C. *Macromolecules* **1999**, *32*, 6172–6179.

troscopy and electron microscopy are used to characterize the three types of particles prior to LbL deposition of CB. The PEI-treated and unmodified PE particles are then compared with respect to LbL film growth using electron microscopy and thermogravimetric analysis (TGA). PE particles containing two to eight bilayers of CB, stabilized with PEI and PAA to provide positive and negative surface charges, were studied. The results indicate that deposition on unmodified or acid etched PE does not produce uniform CB films, and the material that does deposit has variable thickness and poor interfacial adhesion. PEI-grafted PE promotes uniform deposition of CB thin films as evidenced by gravimetric analyses that show a linear increase in weight per bilayer. Composite films, made using compression molding, exhibited a percolation threshold below 0.01 wt % CB and a maximum electrical conductivity of 0.2 S/cm with a concentration of only 6.2 wt % CB. These segregated network composites have among the lowest percolation threshold ever reported with CB as the conductive filler. This combination of surface functionalization and LbL assembly could be used to deposit other types of conductive material or to impart other properties, such as antimicrobial or flame suppression.

2. Experimental Section

2.1. Materials. PEI ($M_n = 10\,000$), poly(methyl vinyl ether-*alt*-maleic anhydride) (Gantrez, $M_n = 1\,130\,000$), ethyl chloroformate (97%), and *N*-methylmorpholine (99%) were purchased from Sigma-Aldrich (Milwaukee, WI) and used as received. Ethylenediamine was purchased from EM SCIENCE (Gibbstown, NJ) and distilled before use. Triethylamine (reagent grade) was purchased from Fisher Scientific (Fair Lawn, NJ) and used as received. PAA ($M_n = 25\,000$) and PEI ($M_n = 100\,000$) which were used for CB stabilization were also purchased from Sigma-Aldrich (Milwaukee, WI) and used as received. Conductex 975 Ultra CB was supplied by Columbian Chemicals (Marietta, GA). This grade of CB has a nitrogen surface area of 242 m²/g, density of 1.8 g/cm³, and a primary particle size of 21 nm. The PE powder used in this study is Fortiflex HDPE J60-800-178, which has a density of 0.96 g/cm³ and an average particle size of 1.7 mm with a very wide size distribution.

2.2. Preparation of PEI/Gantrez Hyperbranched Grafts on Oxidized PE Powder. The PE particle was extracted for 12 h with CH₂Cl₂ in a Soxhlet apparatus and dried at reduced pressure. The PE particle was then oxidized using CrO₃/H₂SO₄/H₂O (1:1:2 by weight) at 90 °C for 1 h, washed with water and acetone, and allowed to air-dry. The oxidized PE particle was then extracted for 12 h with CH₂Cl₂ in a Soxhlet apparatus and dried at reduced pressure.

2.3. Preparation of PEI/Gantrez-Oxidized PE Powder. Oxidized PE powder (10 g) was first activated by treatment with a mixture of ethyl chloroformate (5 mL) and *N*-methylmorpholine (5 mL) in 60 mL of *N,N*-dimethylformamide for 15 min. Next, the powder was isolated by filtration, solution washed with CH₂Cl₂, and allowed to air-dry. The activated PE powder was then placed into a 60 mL solution of CH₂Cl₂ and PEI (branched, $M_n = 10\,000$; 1.5 g) for 1 h. After isolating the PE by filtration and washing it with CH₂Cl₂ and MeOH, the PEI treated PE powder was placed into a solution of triethylamine (10 mL) and of MeOH (60 mL) for 5 min to ensure that any surface ammonium salts were neutralized. The aminated PE was again isolated by filtration, washed with MeOH, and allowed to air-dry. This PEI-treated PE

powder was then placed into 60 mL of tetrahydrofuran (THF) solution of poly(methyl vinyl ether-*alt*-maleic anhydride) (Gantrez, $M_n = 1\,130\,000$; 1.5 g) containing ethylenediamine (28 μ L) for 1 h, isolated by filtration, washed with THF, and allowed to air-dry. The Gantrez-treated PE powder could then be placed into the PEI solution to reform a nucleophilic aminated surface. This cycle of PEI treatment followed by Gantrez treatment was repeated five times to obtain the PEI-6/Gantrez-5 PE powder.

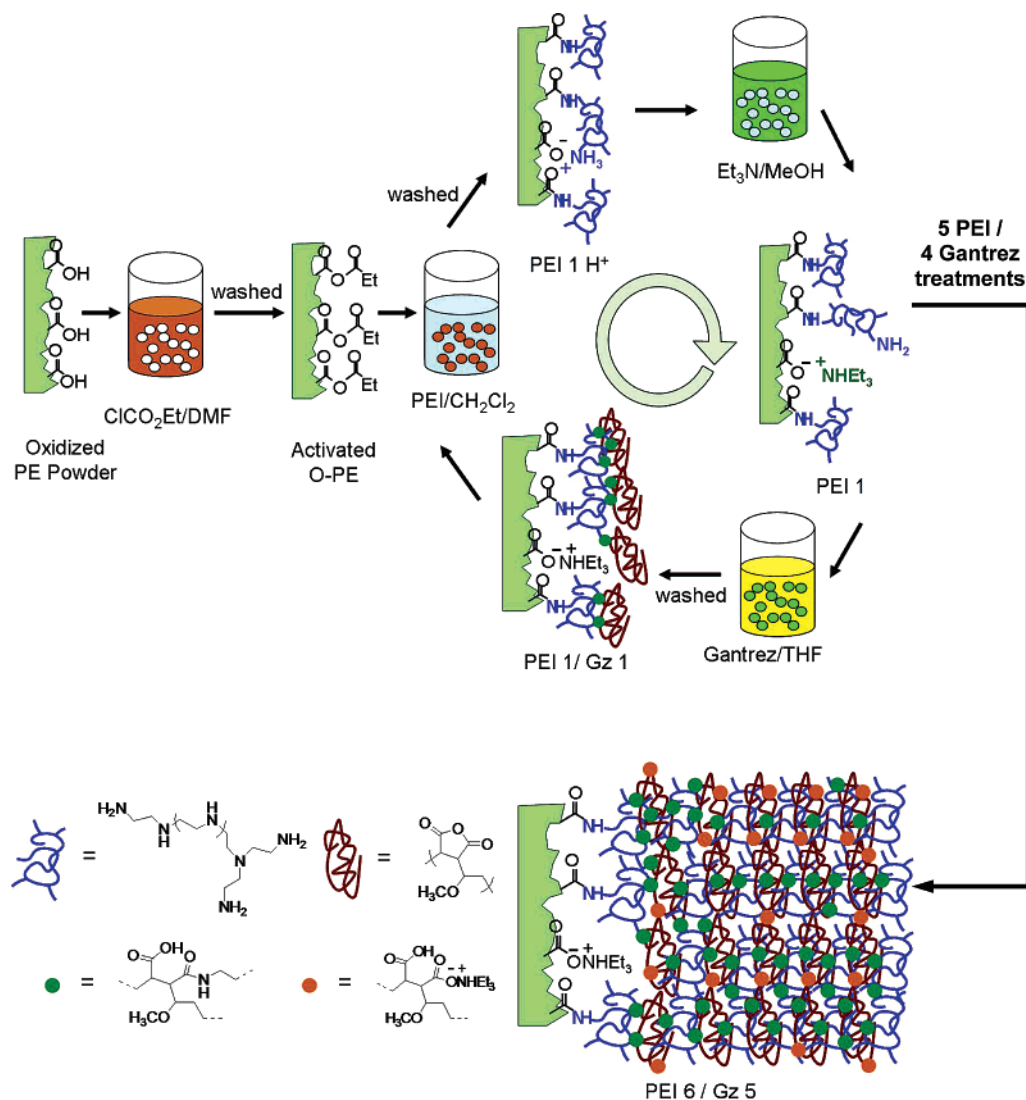
2.4. Film Deposition. Preparation of the CB and polymer mixtures was previously described.¹⁶ PE powder was alternately immersed into aqueous mixtures containing 0.25 wt % CB and 0.05 wt % PEI or PAA. The initial immersion in each mixture was for 5 min followed by 1 min immersions to deposit additional bilayers. Following each immersion the powder was filtered to remove water and excess material. For the PEI-grafted PE powder, the CB–PAA mixture was used first because it were already covered by PEI, but normally CB–PEI would be deposited first. After the deposition was complete, the coated powder was vacuum-dried for more than 24 h to remove residual moisture. Once dried, the powder was compacted in an aluminum mold at 90 °C for 30 min with a pressure of 150 kg/cm². The resulting films are 1.5 mm thick.

2.5. Characterization of the Powder and Coating. Attenuated total reflection–infrared (ATR-IR) spectroscopy was used to confirm growth of the PEI/Gantrez graft on the PE surface. A Bruker Tensor 27 series FT-IR, with a Pike MIRacle ATR accessory at an angle of 45° using a ZnSe crystal, was used. In these spectra, the integrated intensity of the amide peak (1640–1650 cm^{−1}) and carboxylate peak (1550–1560 cm^{−1}) is shown to increase in comparison with the intensity of the underlying bulk polymer C–H absorption (2910 and 2850 cm^{−1}). Titrimetric analysis was carried out by first suspending a weighed amount of the PEI/Gantrez PE powder in a 0.01 M HCl solution and shaking the mixture for 1 h. An aliquot of the resulting HCl solution was titrated with a 0.01 M NaOH solution. In this way, the amount of HCl consumed by basic groups (amine and carboxylate) on the PEI/Gantrez PE powder could then be determined. The average numbers of millimoles of basic groups of PE powder for PEI-1, PEI-2/Gantrez-1, PEI-3/Gantrez-2, PEI-4/Gantrez-3, PEI-5/Gantrez-4, and PEI-6/Gantrez-5 PE particles were 0.0380, 0.2332, 0.3613, 0.5089, 0.6545, and 0.8896 mmol/g of particle, respectively. The concentration of CB on the PE surface was determined using TGA operated from 25 to 900 °C at a rate of 10 °C/min. The conductivities of the compacted films were measured by a home-built four-point-probe system.

3. Results and Discussion

3.1. PEI-Grafted PE. To create a surface amenable to LbL assembly, PE powder was modified according to the steps shown in Scheme 1. First, PE was oxidized by chromic acid. The carboxylic acid groups formed in that oxidation were then activated by ethyl chloroformate to form anhydride groups. A nucleophilic polymer, PEI, was then allowed to react with the anhydrides to form a product where some amine groups of the PEI formed covalent amide bonds and some amine groups of the PEI formed ammonium carboxylates. At this point, the surface was treated with an excess of Et₃N in MeOH. This produced an amine-rich surface that was in turn allowed to react with an electrophilic polymer, poly(methyl vinyl ether-*alt*-maleic anhydride) (Gantrez) to form a new graft with amide linkages. This step produced an anhydride-rich surface because of the excess of anhydride groups that did not react. These steps were repeated several times to yield a hyperbranched hydrophilic surface covered

Scheme 1. Procedure for Covalent LbL Deposition of PEI/Gantrez on the Oxidized PE Particle Surface.



by a network of the PEI and Gantrez polymers with a high functional group loading. Repetition of these steps alternately 6 times with PEI and 5 times with Gantrez produced a grafted product PEI 6/Gantrez 5. This was experimentally a rather simple process much like LbL deposition. The entire surface modification procedure took approximately 12 h.

This covalent step-by-step assembly process is schematically shown in Scheme 1. This artistic picture is not necessarily correct and we suspect that, for example, amine groups from the PEI 1 stage can and do react with Gantrez polymer introduced when forming the PEI 3/Gantrez 3 stage. ATR-IR spectroscopy was used to follow the progress of the grafting chemistry as shown in Figure 1. The oxidized PE had a relatively small peak due to carbonyl groups at 1710 cm^{-1} . After activation and PEI treatment, the acid carbonyl peak disappeared and an amide peak (1650 cm^{-1}) appeared. The Gantrez stages showed anhydride peaks at 1790 and 1730 cm^{-1} , and also a C-O peak ascribed to the methoxyl group around 1100 cm^{-1} . The reaction of PEI and Gantrez to form a mixture of amic acids and ammonium carboxylate groups was confirmed by the disappearance of anhydride peaks and the appearance of amide and carboxylate peaks. Qualitatively, the growth of the grafting layers could

be estimated by comparing the integral of the amide and carboxylate region (1650 and 1560 cm^{-1}) with that of the C-H region from PE itself (2910 and 2850 cm^{-1}). The final PEI-6 had a ratio of about 0.7, whereas the ratio was less than 0.05 with PEI-1.

The PEI/Gantrez covalent assembly process was also monitored by acid-base titration. The results, shown in

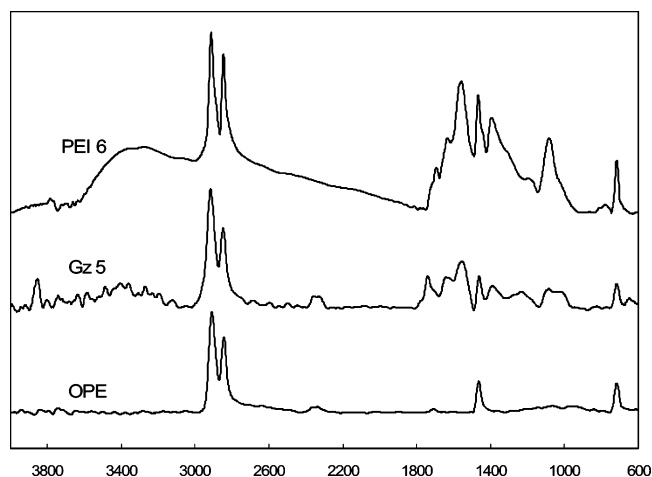


Figure 1. ATR-IR spectra of oxidized PE and PEI/Gantrez PE derivatives.

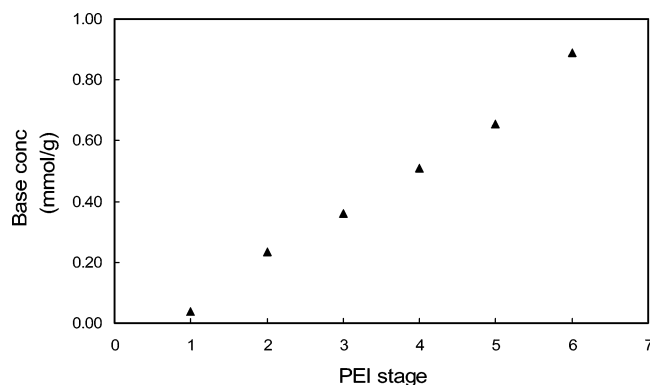


Figure 2. Titrimetric results of PEI/Gantrez PE powders based on three individual experiments.

Figure 2, reveal a linear growth of titratable groups. After six covalent stages of grafting with PEI as the nucleophilic polymer and a mixture of Gantrez with 1.6 wt % ethylenediamine as the electrophilic polymer, the surface loading of the last PEI-6 stage reached 0.89 mmol of basic groups per gram of particle. The PEI-grafted material has a nanoscale texture on the surface while the neat and oxidized PE have smooth surfaces, as shown by the scanning electron microscopy (SEM) images in Supporting Information. PEI is one of the two polymers used to stabilize CB for the LbL assembly, so the grafted particle has an ideal surface.

3.2. CB Coated Powder. PE is a relatively inert, nonpolar polymer that is largely incompatible with the species used for LbL assembly.¹ As shown in Figure 3, CB deposition is very poor on neat PE after two full deposition cycles (i.e., two bilayers of PEI-CB and PAA-CB). The CB layer covers only a small area of an otherwise clean surface. Oxidized PE is not much better after two bilayers, whereas the PEI-grafted surface is completely coated by CB. After four bilayers the coating area increases significantly for the neat PE, but the coating is nonuniform. Some areas are completely covered by the coating while others are completely clean. It appears that spots coated in the previous step act like nucleation sites for subsequent steps. This phenomenon is more clearly shown once six bilayers are deposited, where the boundary of two coating pieces is observed. Each piece of the coating grows as the number of bilayers increases and eventually links together. After eight bilayers, almost all of the area is covered by the CB coating, but boundaries between initial growth sites persist. In addition to poor growth, the CB exhibits poor bonding with the neat PE surface as evidenced by the interfacial gaps shown at eight bilayers. Only a small portion of the coating is weakly attached to the surface by van der Waals attractions and can be easily removed with a small amount of force. Some research groups are actually exploiting this behavior to produce free-standing LbL assemblies.⁶³

Acid oxidation of the surface improves the deposition of CB to some degree. After two bilayers, the oxidized PE shows a surface that is more uniformly speckled with CB than the neat PE particles (see Figure 3). Oxidized PE shows significant improvement over neat PE after four bilayers are

deposited. Furthermore, full surface coverage of the oxidized PE particles is achieved with six bilayers. Much like the situation with neat PE, poor bonding between the oxidized PE and the CB thin film is observed. The interfacial gap shown in Figure 3 at eight bilayers is similar to those seen on neat PE, although thin film uniformity is much improved. Lack of completely uniform growth is believed to be due to surface reorganization that eliminates much of the negative surface charge initially produced during the oxidation process.⁶⁴

Only the PEI-grafted powder demonstrates near perfect compatibility with the LbL process. Unlike the neat and oxidized PE, which show poor initial surface coverage, the PEI-grafted surface is completely covered with just two bilayers of PAA-CB/PEI-CB (see Figure 3). Good interfacial adhesion is also evidenced by the lack of an interfacial gap between the CB thin film and grafted PE. With improved adhesion comes an increase in cracking as the deposited film, containing ~45 wt % CB,¹⁶ attempts to relieve stress. The poor adhesion on the neat PE leads to buckling that is not observed on the PEI-grafted PE. The intermediate deposition and adhesion on the oxidized PE exhibits true cracking, but at six bilayers rather than the four needed on the grafted surface. A linear increase in CB concentration with the number of bilayers deposited suggests that cracking does not adversely affect film growth for the PEI-grafted PE. TGA, shown in Figure 4, qualitatively correlates with the SEM images in Figure 3. The CB concentration of the PEI-grafted particles increases linearly as the number of bilayers is increased, exceeding 6 wt % after eight bilayers are deposited. The CB concentration of neat PE is nearly undetectable at two and four bilayers but increases suddenly at six bilayers. The increasing rate from six to eight bilayers is similar to that of the PEI-grafted case. This result suggests that the CB does not achieve good surface coverage until six bilayers, as shown in the SEM images (see Figure 3). Once the CB layer covers a significant fraction of the surface, additional CB layers can be uniformly deposited because the surface of the support is already covered with complementary material. The CB concentration of the oxidized PE falls between that of the grafted and that of the neat samples. The initial growth is similar to that of the neat PE, but at six bilayers, it becomes more like that of the PEI-grafted PE.

3.3. Segregated Network Films. After deposition, the coated PE powder was compacted at 90 °C for 30 min. Figure 5 shows cross sections of all three films with two and eight bilayers deposited. These images show a segregated network of CB, which is expected to be electrically conductive despite its low concentration of conductive material. During compression, the PE particles lose their roughly spherical shape and become more oblong. The amount of CB, which appears black in these images, correlates well with SEM (see Figure 3) and TGA results (see Figure 4). For neat PE with two bilayers of CB, the network is incomplete because of poor surface coverage. The CB network is much more developed in the film made from oxidized PE and still more enhanced in the film made with

(63) Lutkenhaus, J. L.; Hrabak, K. D.; McEnnis, K.; Hammond, P. T. *J. Am. Chem. Soc.* **2005**, *127*, 17228–17234.

(64) Foldes, E.; Toth, A.; Kalman, E.; Fekete, E.; Tomasovsky-Bobak, A. *J. Appl. Polym. Sci.* **2000**, *76*, 1529–1541.

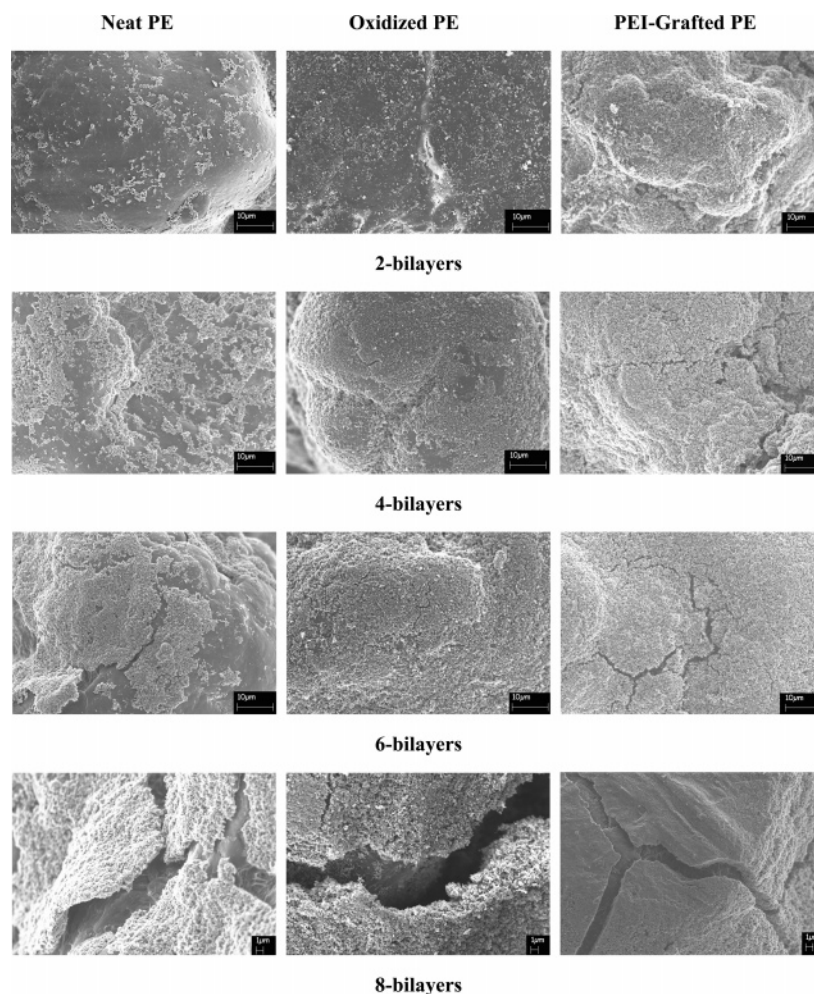


Figure 3. SEM images of neat, acid-oxidized, and PEI-grafted PE particles coated with varying numbers of bilayers of CB stabilized with PAA and PEI.

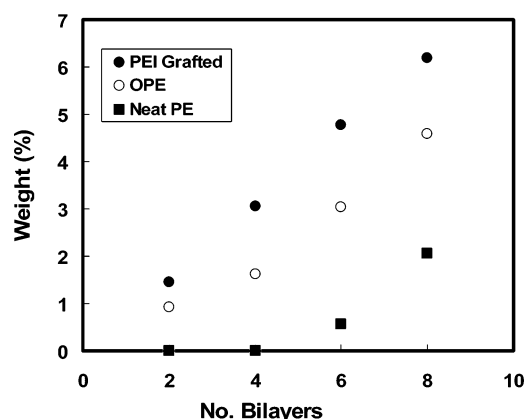


Figure 4. CB concentration as a function of the number of bilayers on PEI-grafted, oxidized, and neat PE particles.

PEI-grafted PE. The microstructure shown for two bilayers on PEI-grafted PE is very comparable to that shown for the neat PE with eight bilayers of CB. Electrical conductivity of these films correlates very well with these microstructures, with better developed networks exhibiting higher conductivity.

During compaction, the large PE particles create excluded volume that keeps CB at the boundaries between them. As a result, the CB coatings create a segregated network structure that reduces the percolation threshold. The percolation threshold is the critical concentration of conductive filler

required to produce measurable conductivity in an insulating matrix. Previous studies have shown that this concentration can be reduced by up to 1 order of magnitude by creating a segregated network.^{54–62} Figure 6a shows the conductivity of compressed films as a function of the number of the bilayers deposited. As expected, films made from PEI-grafted particles exhibit the greatest electrical conductivity. With eight bilayers deposited, conductivity near 0.2 S/cm is achieved. On the basis of TGA results (see Figure 4) this corresponds to a CB concentration of just 6 wt %. Composites made using traditional melt processing required more than 30 wt % of the same high structure CB to obtain a comparable resistivity in HDPE.⁶⁵ Films made with neat PE particles do not exhibit measurable conductivity until six bilayers of CB are deposited, and this value (~ 0.002 S/cm) is more than 1 order of magnitude lower than that of the PEI-grafted film (~ 0.07 S/cm). The films made from oxidized PE particles show electrical conductivity that is more similar to that of the grafted particles than that of the neat PE, exhibiting measurable conductivity at all bilayers. Despite showing a similar trend of increasing conductivity with number of bilayers, the oxidized particle films are significantly less conductive than the grafted films at all bilayers (see Table S1 in Supporting Information). The

(65) Yu, J.; Zhang, L. Q.; Rogunova, M.; Summers, J.; Hiltner, A.; Baer, E. *J. Appl. Polym. Sci.* **2005**, *98*, 1799–1805.

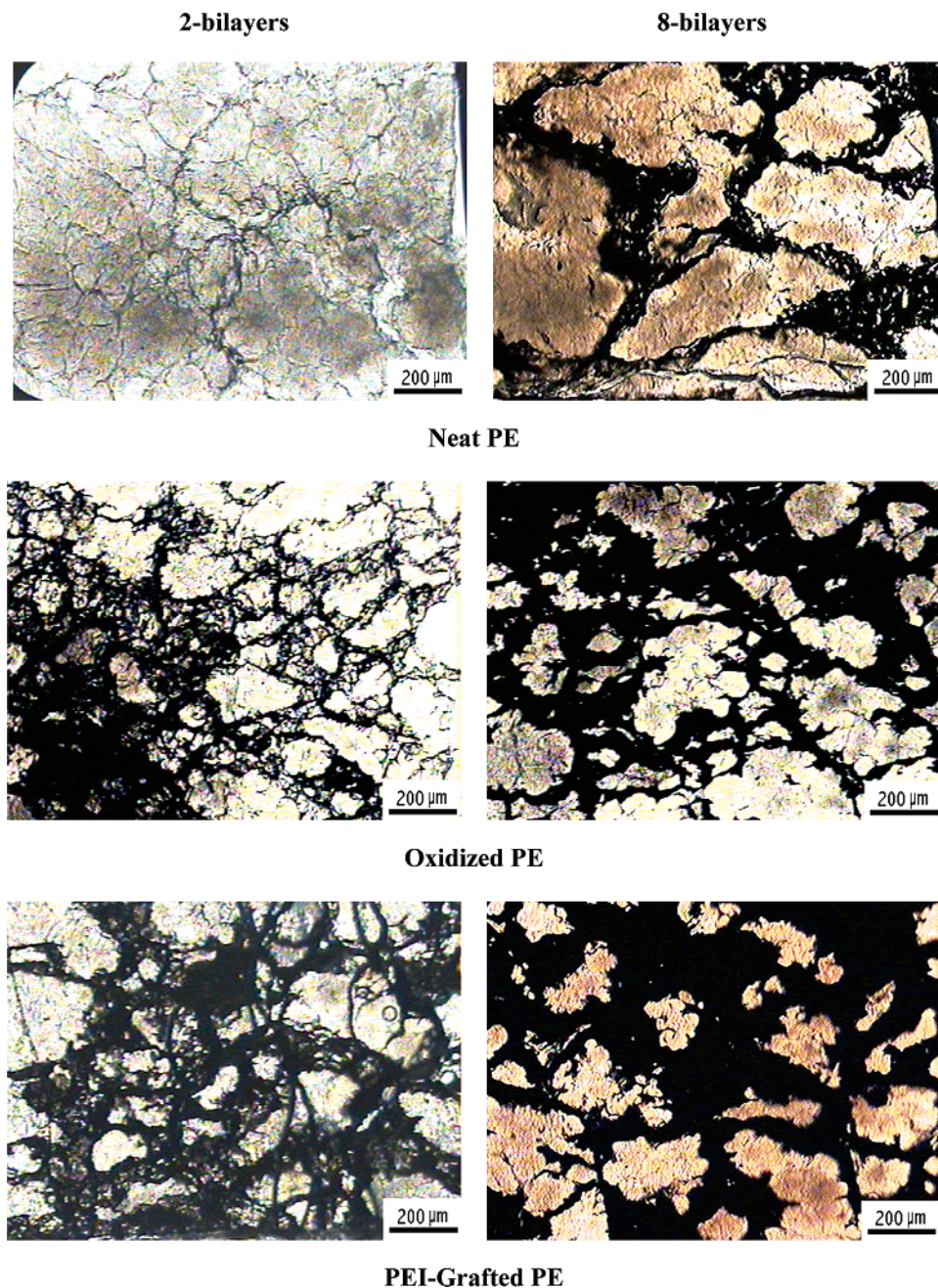


Figure 5. Optical microscope cross sections of compressed films made with neat, acid-oxidized, and PEI-grafted PE particles containing two and eight bilayers of CB stabilized with PAA and PEI.

difference in film behavior between oxidized PE and PEI-grafted PE is more pronounced when conductivity is shown as a function of CB concentration.

Using the TGA data from Figure 4, the number of bilayers in Figure 6a can be converted to CB concentration to generate percolation-style curves for the films made with oxidized and PEI-grafted particles. Figure 6b shows these data fitted with the classical percolation power law⁴⁹

$$\sigma = \sigma_0(V - V_c)^s \quad (1)$$

where σ is the measured conductivity, σ_0 is a scaling factor, V is the volume fraction of CB, V_c is the percolation threshold, and s is the power law exponent. The PEI-grafted PE films have a percolation threshold of 0.085 wt % CB, while the oxidized PE films have a percolation threshold that is 1

order of magnitude higher at 0.88 wt %. Melt processed composite films made with the same CB and PE of the same density show a percolation threshold of 13.5 wt %.⁶⁵ It is clear that the segregated network microstructure generated in the compacted films is able to shift the percolation threshold by more than 1 order of magnitude. The order of magnitude difference between the two surface treatments suggests that the deposition is less uniform in the case of the oxidized PE particles, as evidenced by comparing the SEM images in Figure 3. Both systems converge near 3 wt % CB, but this concentration is achieved at four bilayers for the grafted particles and six bilayers for the oxidized particles. This combination of low percolation threshold and relatively high electrical conductivity, especially for the PEI-grafted system, is currently the best reported for a CB-filled polymer composite.

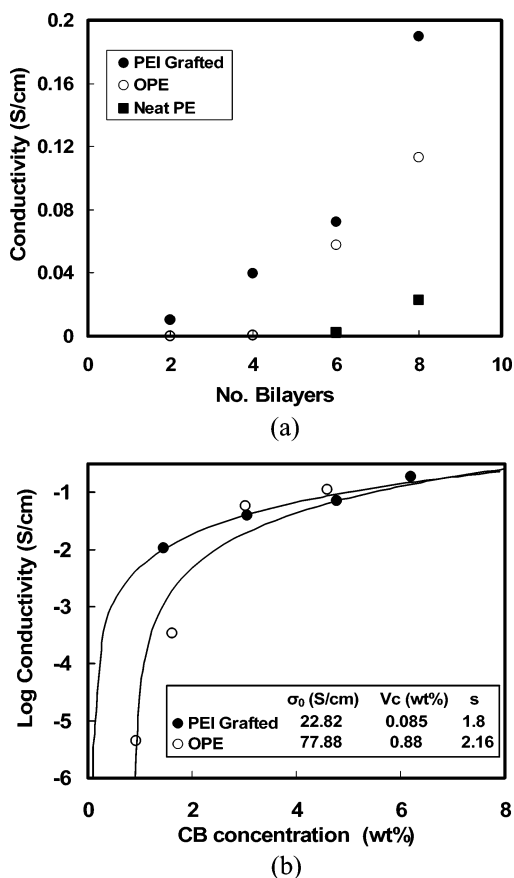


Figure 6. Electrical conductivity as a function of the number of the bilayers (a) and CB concentration (b) for films made by compression molding PE particles following LbL deposition of CB.

4. Conclusion

The effects of no treatment, surface oxidation, and covalent grafting of PEI on PE particles were compared with respect to growth and adhesion of CB thin films deposited using LbL assembly. In the absence of surface modification, LbL

film growth is patchy and adhesion is very poor. Surface oxidation improves the rate of film growth; however, it still lacked uniformity at small numbers of bilayers, and adhesion remained weak. Grafting multiple layers of PEI to the PE powder surface provided excellent coverage and promoted stable LbL film growth and excellent adhesion. This CB coated powder was compression molded into films, and their conductivity was measured, which revealed a percolation threshold below 0.01 wt % CB for the PEI-grafted system. Electrical conductivity of 0.2 S/cm was achieved with only 6 wt % CB, which is exceptional for a CB-filled PE film. Modification of deposition parameters, such as the ratio of stabilizer to CB, may further increase conductivity and/or reduce the percolation threshold of these films. The use of surface grafting in combination with LbL deposition could be used to impart other useful properties to polyolefin films or particles, including antimicrobial or flame retardant behavior. These initial results demonstrate the ability to use LbL assembly on a substrate that is traditionally incompatible with this water-based technology. It is difficult to quantitatively assess the improvement in thin film adhesion that occurs with surface grafting. Future work will seek to measure interfacial adhesion and evaluate the effects of different grafting techniques and polymers.

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Supporting Information Available: SEM images of neat, oxidized, and PEI-grafted PE particles and a table of electrical conductivity data for Figure 8 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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