

**LAYER-BY-LAYER ASSEMBLY OF ELECTRICALLY
CONDUCTIVE POLYMER THIN FILMS**

A Thesis

by

CHIEN SY JASON JAN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2006

Major Subject: Mechanical Engineering

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Approved by:

Chair of Committee,
Committee Members,

Head of Department,

Jaime Grunlan
Hung-Jue Sue
Zoubeida Ounaies
Dennis O'Neal

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ABSTRACT

Layer-by-Layer Assembly of Electrically

Conductive Polymer Thin Films. (May 2006)

Chien Sy Jason Jan, B.S., The University of Texas at Austin

Chair of Advisory Committee: Dr. Jaime Grunlan

Layer-by-layer (LbL) assembly was used to produce highly conductive thin films with carbon black (CB) and polyelectrolytes. The effects of sonication and pH-adjustment of the deposition mixtures on the conductivity and transparency of deposited films were studied. Drying temperature was also evaluated with regard to thin film resistance. Sonication and oven drying at 70°C produced films with the lowest sheet resistance ($\sim 1500 \Omega/\text{sq}$), which corresponds to a bulk resistivity of $0.2 \Omega\text{-cm}$ for a 14-bilayer film that is $1.3 \mu\text{m}$ thick. Increasing the pH of the PAA-stabilized mixture and decreasing the pH of the PEI-stabilized mixture resulted in films with 70% transparency due to thinner deposition from increased polymer charge density. Varying the number of bilayers allows both sheet resistance and optical transparency to be tailored over a broad range.

Variation of deposition mixture composition led to further reduction of sheet resistance per bilayer. A 14 bilayer film, made from mixtures of 0.25wt% carbon black in 0.05wt% PAA and plain 0.1wt% PEI, was found to have a sheet resistance of approximately $325 \Omega/\text{sq}$. Bulk resistivity was not improved due to the film being $8 \mu\text{m}$ thick, but this combination of small thickness and low resistance is an order of

magnitude better than carbon black filled composites made via traditional melt or solution processing. Applications for this technology lie in the areas of flexible electronics, electrostatic charge dissipation, and electromagnetic interference shielding.

DEDICATION

To my family

ACKNOWLEDGEMENTS

First and foremost I would like to thank my family, namely my mother and father who have been and always will be there for me no matter what. My educational opportunities are a tribute to my parent's hard work and dedication, never allowing me to settle and pushing me to maximize my potential. They have given so much to me that I can never fully repay them.

Secondly I would like to thank my committee chair, Dr. Jaime Grunlan for his continued support and encouragement throughout the entirety of my academic and research career here at Texas A&M University. I would also like to thank my committee members, Dr. Hung-Jue Sue and Dr. Zoubeida Ounaies for being supportive members of my committee during my tenure here at Texas A&M University.

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CHAPTER I

INTRODUCTION

Layer-by-layer (LbL) assembly is a procedure that utilizes mutual attractions between deposited species (e.g., electrostatic, covalent, hydrogen-bonding, etc.) to build thin films onto a substrate [1,2]. This technique has garnered much attention in recent years for the ability to create functional multilayer thin films for a wide variety of applications. The ability to assemble complex structures and tune macroscopic properties on the nano scale using this simple process is very powerful. LbL thin films have a wide range of applications including graded semiconductors for optoelectronics [3], solid electrolytes for batteries [4], degradable encapsulation [5], anti-reflection coatings [6], and controlling cell growth [7]. In the present study, thin films of carbon black have been created to produce highly conductive surfaces with tunable behavior.

Pioneering work by Irving Langmuir and Katherine Blodgett in 1927, laid the foundation for modern LbL film deposition. The Langmuir-Blodgett technique showed that monolayers could be deposited on the surface of water by applying pressure, undergoing phase change from the gaseous to the solid state [8]. Once deposited on the surface of the water, the monolayers could be transferred to a rigid substrate by passing the substrate through the air-water interface [9].

The thesis follows the style of Carbon.

Multilayers were then achieved by the repetitive dipping through the air-water interface as the monolayers would naturally build upon themselves. The Langmuir-Blodgett technique was the first technique to give chemists the ability to construct ordered molecular assemblies that are both highly ordered and uniform in thickness. Despite significant progress, this technique is very limited when it comes to film quality and stability resulting in very few applications [10,11].

The modern LbL process, used in the present work, is based on the technique developed by Iler et al. in 1966 [12]. He presented a technique for building films with uniform thickness by the alternate adsorption of oppositely charged colloidal particles [12]. Decher et al. extended this technique by using proteins, polymers, and nanoparticles [13]. Some key advantages of the LbL process over other coating methods include the ability to, control coating thickness down to the nanometer (nm) level, easily insert variable thin layers without altering the process, economically use raw materials (due to thin nature), self-heal, and process under ambient conditions.

Thin films, typically $< 1 \mu\text{m}$ thick, are often created by alternately exposing a charged substrate to polyanionic and polycationic polymer solutions and aqueous mixtures. The exposure is done by submerging the substrate into solutions with consistent time of dipping between the polyanionic and polycationic solutions. Having numerous charges on each molecule creates a charge reversal on the surface which causes repulsion of similarly charged molecules and limits the growth to a single layer at a time [14]. Figure 1 schematically shows the process used to generate LbL thin films. Figure 2 shows the results of the deposition process as the layers build upon themselves

and the solid substrate. Each deposited positive-negative pair (consisting of two individual species) is referred to as a bilayer and is typically 1 – 100+ nm thick depending on chemistry [15], molecular weight [16], temperature [17], counterion [18], ionic strength [19], and pH [20]. The LbL process is also very conformable, making it useful for adding functionality to complex substrates (e.g., fabric or foam) that cannot be accomplished with traditional coating techniques.

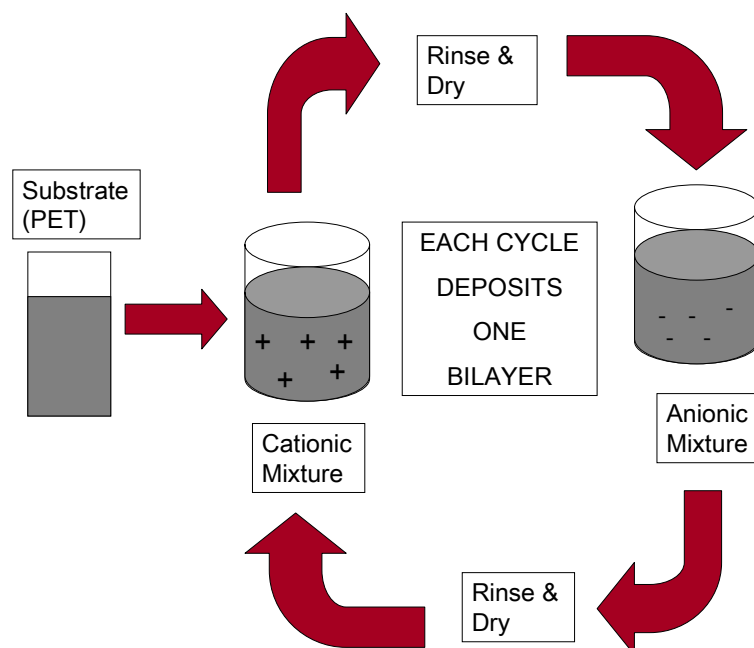


Figure 1. Layer-by-layer deposition process.

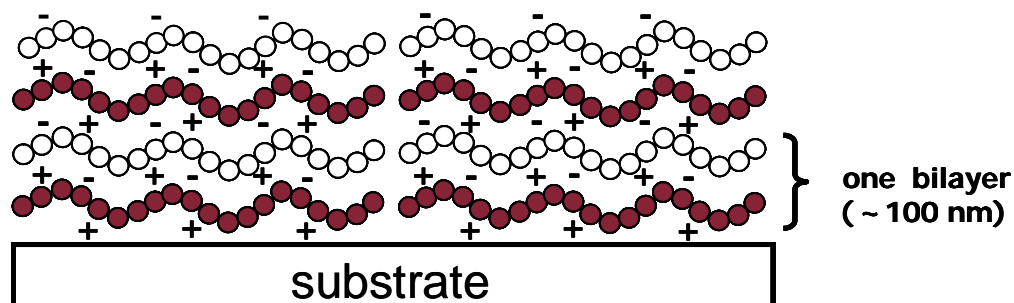


Figure 2. Film growth using LbL technique, showing bilayer deposition on a general substrate.

During LbL film assembly, the electrostatic attractions between positively and negatively charged molecules or particles allow the films to grow. Inherently, polyelectrolytes are ideal macromolecules for the self-assembly process since they are charged molecules that can be either positively or negatively charged and are easily mixed into an aqueous solution. In solution, the ionic groups dissociate into polyions and other smaller ions [21]. The resulting polyanions and polycations are then used for the LbL self assembly process. Polyelectrolytes are broken down into two categories, strong or weak, depending on the degree of dissociation in aqueous media. Strong polyelectrolytes fully dissociate in aqueous solutions over the entire pH range. This occurs because of the strong acid and base groups attached to each of the polymer repeat units [21]. In weak polyelectrolytes, the ionization of the polyelectrolytes in solution is dependent on the pH of the solution [22-24]. Polyelectrolytes can be combined with colloidal particles, such as carbon black, to impart functionality to a given multilayer. Figure 3 shows the range of charge density available in water-soluble polymers.

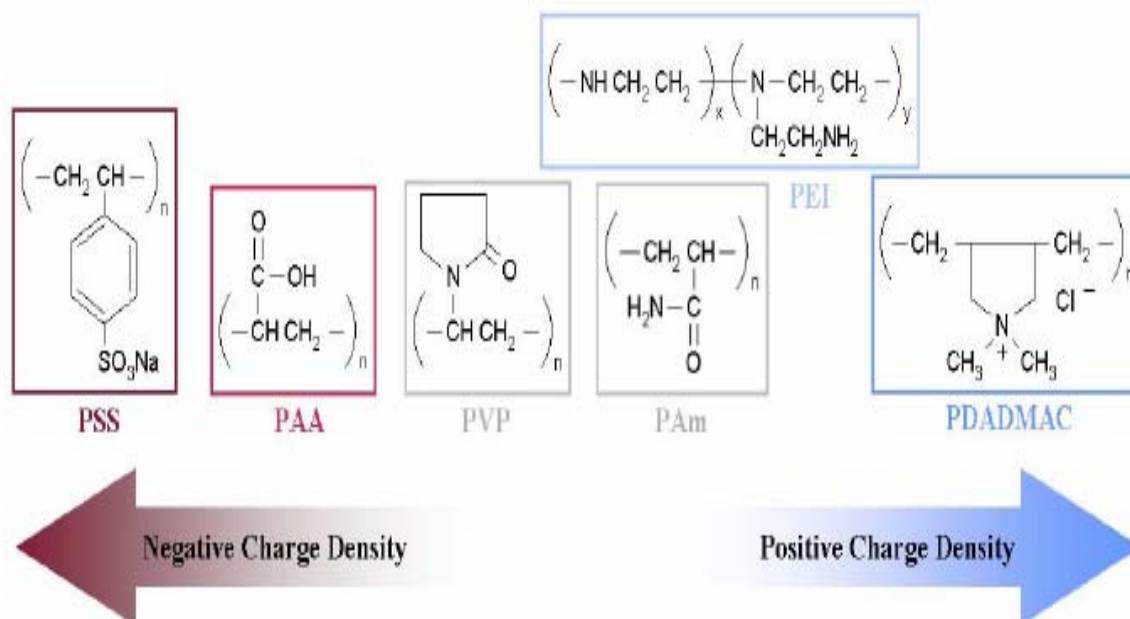


Figure 3. Diverse range of water-soluble polymers under neutral conditions.

Carbon black is a colloidal, amorphous material that has a structure similar to disordered graphite [25]. Figure 4 shows the general size and structure of carbon black particles. Carbon black is typically used as reinforcing filler with the following applications: (1) dimensional stabilizer, (2) conductive filler, (3) antioxidant, and (4) pigment [25]. For carbon black to be an effective conductive filler, small particle diameter and large surface area is desired. The process which creates this type of carbon black is termed the furnace process in which oil is thermally decomposed to form fluffy carbon black particles with the proper physical characteristics [26].

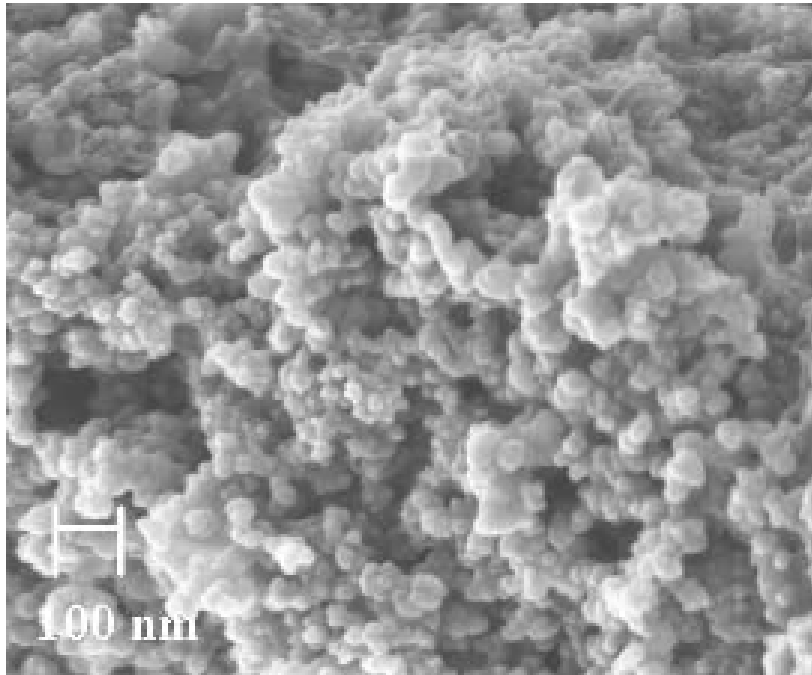


Figure 4. SEM image showing carbon black particle size and shape.

When used as conductive filler in polymer composites, there are three important properties of carbon black that need to be taken into consideration: (1) particle size (including surface area), (2) structure, and (3) surface chemistry [26-29]. High surface area and high porosity are both critical characteristics of carbon black when used to impart electrical conductivity in polymer composites [25]. Increasing the surface area of the carbon black particles in the polymer composites decreases the gaps between the polymer and the conductive aggregates thus promoting a conductive network [25]. Carbon black consisting of chainlike aggregates, composed of primary particles with extensive branching, is considered to be high structure. High structure carbon black has strong attractive forces between the aggregates, resulting in larger aggregates being in contact with each other and smaller distances between aggregates promoting the formation of conductive networks [30]. Surface chemistry refers to the amount of

volatile content found on the surface of the carbon black. The amount of volatile content is determined by measuring the percent weight loss of carbon black after being heated for 7 minutes at a temperature of 950°C [30]. To achieve high levels of conductivity using carbon black and polymer composites, the optimal characteristics are high surface area, high structure, and low volatile content [25]. The high structure carbon black (trade name, Conductext 975 Ultra) used in this study was provided by Columbian Chemicals (Marietta, GA). Conductex carbon black has a primary particle size of 21 nm and a nitrogen surface area of approximately 5500 nm² making it an ideal filler for conductive composites.

Melt mixing [31-33] and solution processing [34,35] are the most common techniques used to produce electrically conductive composites with carbon black. These types of polymer composites have been studied for use as temperature [36,37] and chemical sensors [37-39], electrostatic dissipation (ESD) layers [40,41], and electromagnetic interference (EMI) shielding [40,42]. In many cases, a significant concentration of carbon black (> 25wt%) is required to achieve the necessary level of conductivity. These high carbon black concentrations produce high mixing viscosity and brittle composite films with extensive porosity due to aggregated filler [43,44]. The LbL process avoids these problems by using dilute mixtures (< 1 wt% solids) to deposit layers of carbon black that are pre-stabilized with polyethylenimine (PEI) and poly(acrylic acid) (PAA) (see chemical structures in Fig. 3). The resulting films are thin, flexible, and relatively dense, with a high concentration of carbon black (> 40wt %). In the present study, sheet resistance and optical transparency is tailored by changing the

number of bilayers, the pH of aqueous deposition mixtures, sonication of the mixtures, oven treatment, and composition of deposition mixtures. Multiplying sheet resistance by film thickness shows these films to have bulk resistivity well below thick composites made using traditional techniques, making them useful for a variety of sensing, shielding, and flexible electronics applications.

The following chapters describe carbon black filled polymer composite thin films made using the LbL process. Electrical conductivity is the key property used to study changes in these films as processing and composition were altered. Two different sets of experiments were conducted. Chapter II describes experiments involving processing variables. The effects of sonication, oven treatment, and pH-treatment are evaluated with respect to film conductive and optical behavior. Chapter III focuses on compositional variables. Electrical conductivity is evaluated as the composition of deposition mixtures is varied. Chapter IV highlights the significance of the experimental results as they pertain to real world applications. There is a specific example of a bulk composite made by applying carbon black LbL to large polyethylene (PE) particles that were then compression molded. Chapter V is a summation of the work done for the present study and key conclusions.

CHAPTER II

PROCESSING VARIABLES

In this study, three processing variables were evaluated: (1) deposition mixture sonication, (2) oven treatment of deposited films, and (3) deposition mixture pH adjustment. Adjusting these variables produced changes in the sheet resistance of the resulting composite films. The goal was to minimize sheet resistance and/or visible light absorbance. Significant tailoring of final film properties is possible with these key variables, as shown below. The effect of changing carbon black and polymer composition within the deposition mixtures is described in Chapter III.

Materials and Methods

Materials

Two types of polymers were used to stabilize carbon black for layer-by-layer (LbL) assembly of composite thin films. Poly(acrylic acid) (PAA) and polyethylenimine (PEI) were purchased from Aldrich (Milwaukee, WI). PEI is a weak polycation with a molecular weight of 25,000 g/mol, while PAA is a weak polyanion with a molecular weight of 100,000 g/mol. Both polymers were used as supplied without further purification. Poly(ethylene terephthalate) (PET) film (trade name Melinex ST505), with a thickness of 175 μm , was purchased from DuPont-Teijin Films (Hopewell, VA) and used as the substrate for deposition. Conductex 975 Ultra carbon black (CB) was supplied by Columbian Chemicals (Marietta, GA). This grade of conductive carbon black has a nitrogen surface area (NSA) of 242 m^2/g and a primary particle size of 21 nm.

Carbon Black Mixture Preparation

PEI and PAA were added to de-ionized water to produce solutions containing 0.05wt% polymer. These solutions were then rolled for at least 12 hours on a Cell-Production Roller Apparatus by BELCO Biotechnology (Vineland, NJ) with a rotation speed of approximately 4 rpm to achieve equilibrium. Carbon black was then added to each solution at a concentration of 0.25wt% using a high speed impeller for 15 minutes at 3600 rpm, followed by rolling for 12 hours to achieve equilibrium. Finally, these equilibrated mixtures were either sonicated and/or pH treated or otherwise unaltered prior to use. Sonication, if done, was for 15 minutes in a Bransonic Tabletop Ultrasonic Cleaner by Branson (Danbury, CT). When pH treating, the CB-PEI mixture was decreased to 7 and the CB-PAA mixture was raised to 5 using 1M HCl and 1M NaOH, respectively.

Film Deposition

Prior to deposition, the PET substrate was cut to the desired size, approximately 2.5 inches by 4 inches, followed by rinsing with methanol and de-ionized water to remove grease, dust, and other possible impurities. Cleaned substrates were then corona treated using a BD-20C Corona Treater (Electro-Technic Products Inc., Chicago, IL) to oxidize the surface [45,46]. After the corona treatment, the PET was initially dipped in the CB-PEI aqueous mixture for 5 minutes, followed by rinsing with de-ionized water and blow drying with nitrogen or air. The same procedure was followed with the CB-PAA mixture to complete the initial bilayer. Each subsequent bilayer was dipped for one minute in each of the mixtures, followed by the same rinsing and drying procedure.

Figure 1 (in Chapter I) shows a schematic summary of this deposition process. Most films were hand-dipped, but films requiring 20 or more bilayers were made with the home-built robot, shown in Figure 5, specifically constructed to use for the LbL process [47]. Once deposited, some films were dried via an oven for 15 minutes while some were left to dry in ambient conditions. All films were stored in ambient conditions away from dust, dirt, and other possible impurities for at least 12 hours prior to testing.

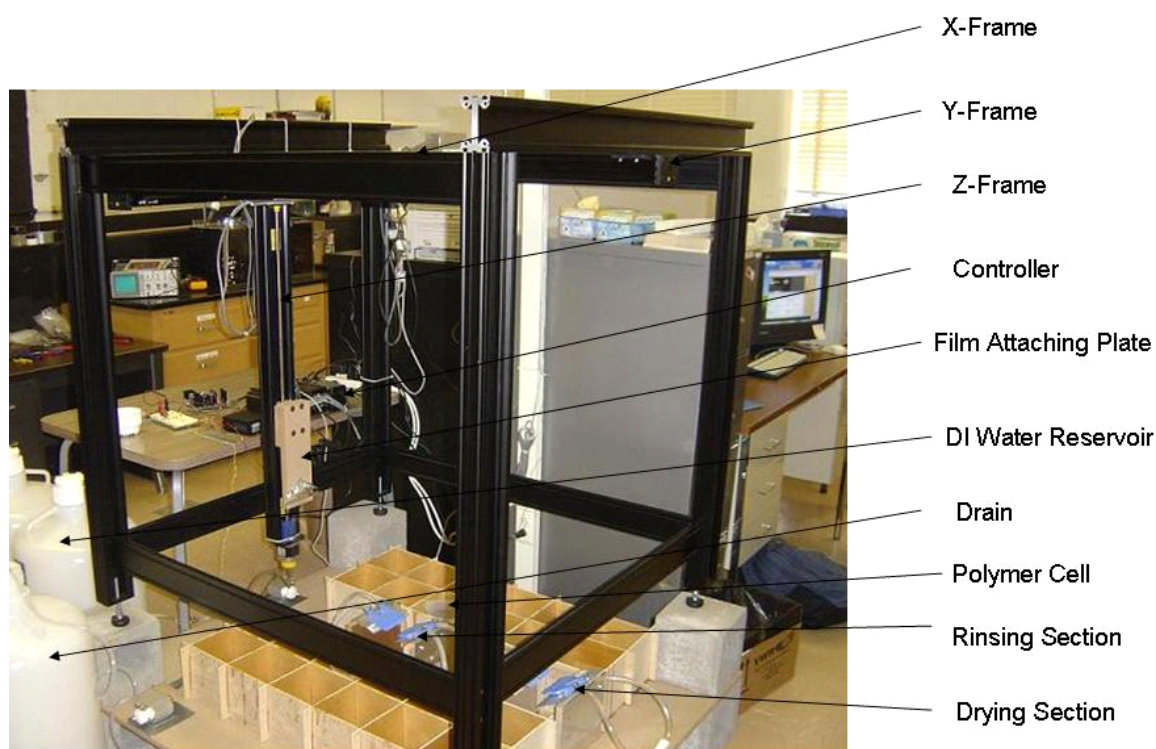


Figure 5. Three-dimensional robot capable of depositing thin films in LbL fashion. A substrate is dipped into a solution, rinsed, dried, and then dipped into the next solution then the process repeats [47].

Film Characterization

Sheet resistance of the carbon black films was measured with a home-built four-point probe (FPP) apparatus. An Agilent power supply and Keithley multimeter with a

Signatone probe head were used in conjunction with LabView software to operate the apparatus. Optical transparency was measured with a Cary 100 UV-vis spectrophotometer (Varian, Inc., Palo Alto, CA). Absorbance of the films was measured between the wavelengths of 200 and 900 nm. Thermogravimetric analysis (TGA) was used to determine the concentration of carbon black in the deposited films. Composite weight loss as function of temperature was determined using a TA Instruments Q600 TGA (New Castle, DE) operated from 25°C to 900°C at a rate of 10°C per minute. Thickness of the films was found using a Daktek 3 profilometer (Veeco Instruments Inc., Woodbury, NY). Surface images of the films were obtained using a Zeiss 1530 VP FE-SEM (Carl Zeiss, Inc., Thornwood, NY) and cross-sections were imaged with a JEOL 1200EX TEM (JEOL USA, Inc., Peabody, MA).

Results and Discussion

Depositing carbon black using the LbL process with the aid of weak polyelectrolytes (PEI and PAA) yields composite thin films with tunable sheet resistance and optical transparency. As shown below, many of the resulting films are less than 1 μm thick and have bulk resistivity (the product of sheet resistance and film thickness) below 1 $\Omega\cdot\text{cm}$. Traditional carbon black-filled polymer composites rarely achieve resistivity below 10 $\Omega\cdot\text{cm}$ [31, 35, 48-50]. Low resistivity in the LbL films is the result of high carbon black concentration (average of 45wt% based on TGA data) and the fact that these films are dense, as shown in TEM cross-sections. Figure 6 shows a representative weight loss profile that demonstrates how carbon black concentration was

determined. Carbon black concentration was found by taking the wt% left after the polymer and excess water had been burned out and dividing it by the wt% after water had been removed. This level of carbon black is very difficult to achieve in a glassy composite using traditional processing techniques and the resulting composites are very brittle and porous [43]. The effects of sonication and pH adjustment of the deposition mixtures and oven treatment of deposited films are evaluated here. In all cases sheet resistance decreases as the number of bilayers increases, but the values and amount of change between bilayers is influenced by the parameters just mentioned.

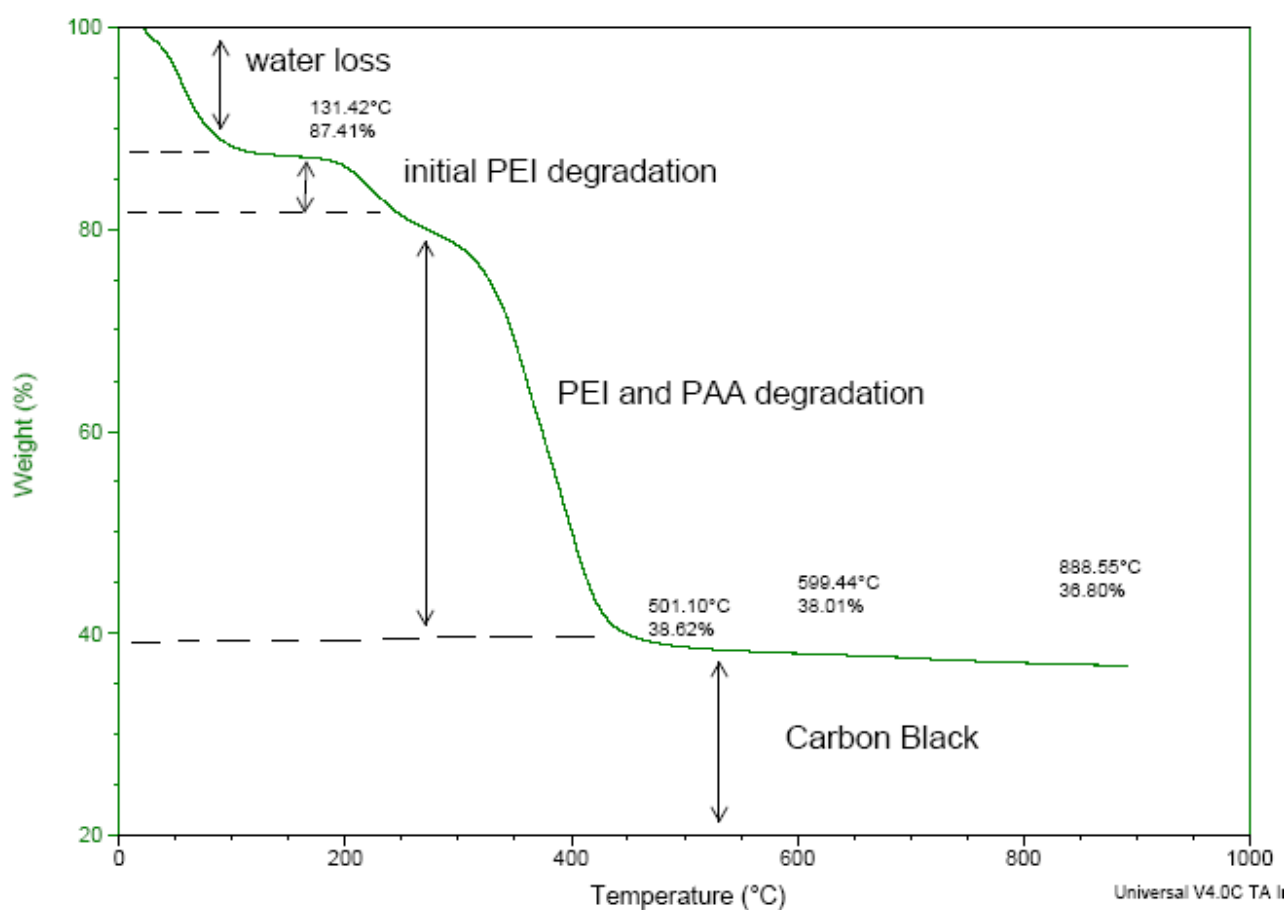


Figure 6. TGA data showing the concentration of carbon black in the LbL films.

Sonication Effects

Sonicated of the carbon black and polymer aqueous mixtures prior to film deposition reduces the sheet resistance of the resulting carbon black films, as shown in Figure 7. Non-sonicated mixtures result in films with greater sheet resistance than those produced from sonicated mixtures.

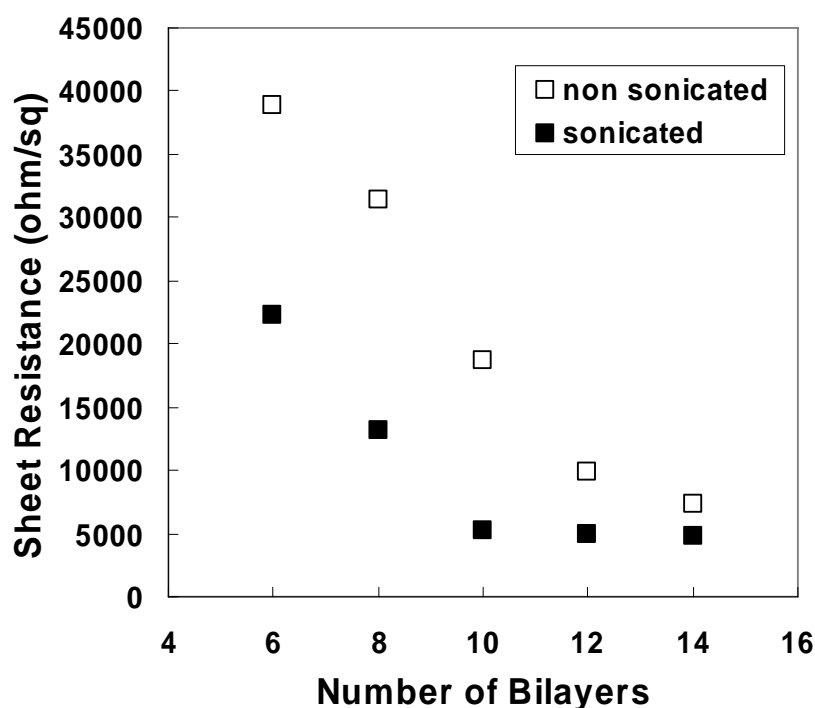


Figure 7. Sheet resistance values comparing sonicated films and non-sonicated films. Standard deviation for these two data series is less than 8% for all values.

Both sets of films show a linear increase in film thickness with each deposited bilayer. The sonicated films are slightly thicker than the non-sonicated films, but this difference is not enough to account for the sheet resistance values that are often more than 100% different. The trend of film thickness can be seen in Figure 8. Sonication

breaks up carbon black aggregates held together with van der Waals attractions [51] without affecting individual carbon black particles, which results in a finer distribution of particles for LbL deposition. One theory assumes that the smaller, more uniform particles will pack more efficiently and result in a more conductive film, but other factors to explain this phenomenon are possible. The slope is the same for both sets of films (~125nm per bilayer), which suggests the sonicated mixtures achieve full coverage of the substrate with fewer layers than the non-sonicated mixtures.

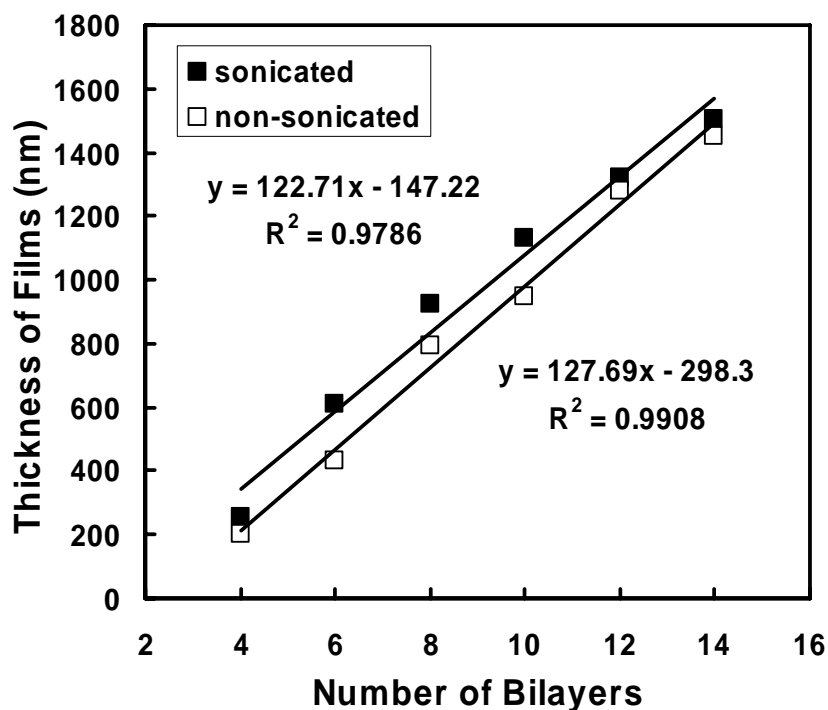


Figure 8. Film thickness values comparing sonicated films and non-sonicated films. Standard deviation for all thickness values less than 10%.

Sonicated films achieve a minimum bulk resistivity of 0.6 $\Omega\cdot\text{cm}$, while non-sonicated films reach a minimum of approximately 1 $\Omega\cdot\text{cm}$. Bulk, or slice, resistivity is

the product of sheet resistance and film thickness. Figure 9 shows the difference in bulk resistivity and Table 1 compares both sheet resistance, thickness, and bulk resistivity between sonicated and non-sonicated films. Both the sonicated and non-sonicated films show a linear decrease in sheet resistance with increasing number of bilayers, but the linearity levels off beyond 10-bilayers despite a continued increase in film thickness. This diminishing reduction of sheet resistance is due to sub-micron cracks that begin to form at 10-bilayers and continue to grow with additional layers.

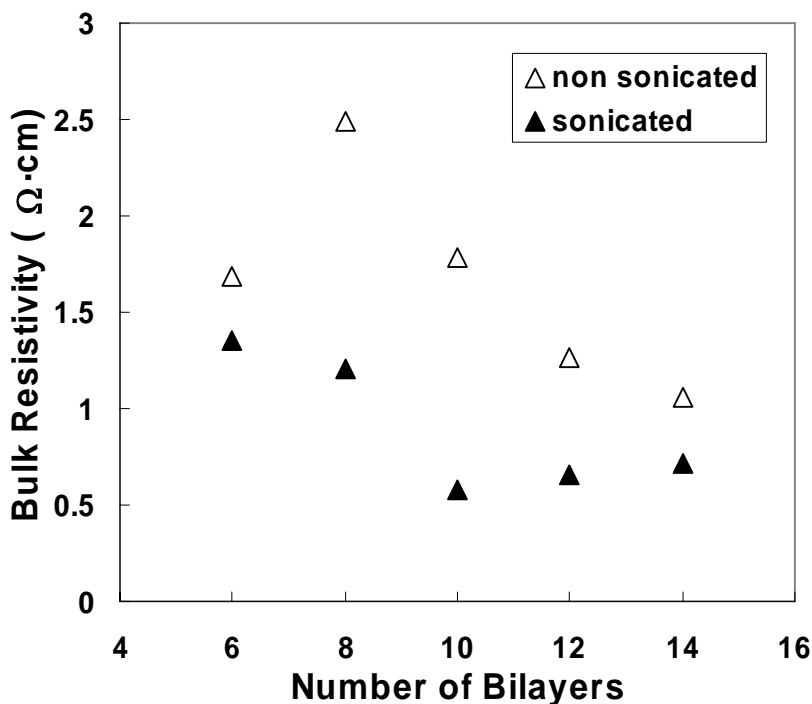


Figure 9. Bulk resistivity values comparing sonicated films and non-sonicated films.

Table 1

Thickness, sheet resistance, and bulk resistivity for carbon black thin films made with different processing variables.

0.25% CB in 0.05% PEI and PAA, non-sonicated, no pH treatment, no oven treatment			
Bilayers	Thickness (nm)	Sheet Resistance (Ω/sq)	Bulk Resistivity (Ω·cm)
4	198.75	N/A	N/A
6	434.76	38907.03	1.69
8	795.12	31337.14	2.49
10	949.76	18733.12	1.78
12	1276.85	9887.69	1.26
14	1450.23	7311.67	1.06
0.25 % CB in 0.05% PEI and PAA, sonicated, no pH treatment, no oven treatment			
Bilayers	Thickness (nm)	Sheet Resistance (Ω/sq)	Bulk Resistivity (Ω·cm)
4	255.84	358987.90	9.18
6	607.75	22244.34	1.35
8	923.00	13096.23	1.21
10	1131.02	5167.70	0.58
12	1321.71	4988.73	0.66
14	1503.84	4806.31	0.72
0.25% CB in 0.05% PEI and PAA, sonicated, no pH treatment, oven treatment			
Bilayers	Thickness (nm)	Sheet Resistance (Ω/sq)	Bulk Resistivity (Ω·cm)
4	255.21	28476.94	0.73
6	456.70	10425.34	0.48
8	806.18	4929.52	0.39
10	888.33	2978.68	0.26
12	1206.78	1948.87	0.24
14	1321.16	1515.79	0.20
0.25% CB in 0.05% PEI and PAA, sonicated, pH treatment, no oven treatment			
Bilayers	Thickness (nm)	Sheet Resistance (Ω/sq)	Bulk Resistivity (Ω·cm)
4	N/A	N/A	N/A
6	255.54	N/A	N/A
8	238.19	110343.07	2.63
10	341.15	31699.00	1.08
12	575.09	12066.43	0.69
14	621.39	10466.37	0.65

Table 1
Continued.

0.25% CB in 0.05% PEI and PAA, sonicated, pH treatment, oven treatment			
Bilayers	Thickness (nm)	Sheet Resistance (Ω/sq)	Bulk Resistivity ($\Omega\cdot\text{cm}$)
4	N/A	N/A	N/A
6	208.29	N/A	N/A
8	N/A	72718.16	N/A
10	253.12	26667.56	0.67
12	N/A	7279.83	N/A
14	351.09	6171.79	0.22

* Standard deviation for all thickness values less than 15%, standard deviation for sheet resistance values less than 10%.

Surface images were taken using a scanning electron microscope (SEM). These surface images show that after a certain number of bilayers are deposited, (~12), cracks begin to form within the films. The following series of figures show SEM images comparing varying bilayers of non-sonicated and sonicated films. Surface images of 6-bilayer films in Figures 10 and 11 shows greater uniformity in the sonicated film as expected. The 14-bilayer film shown in the same figures highlights the cracking that occurs beyond 10-bilayers, as indicated by the non-linearity in sheet resistance as a function of bilayers (see Fig. 8). Under these processing conditions the cracks are difficult to discern, but cracks are very apparent when oven treatment is used. As the number of bilayers continues to increase, sheet resistance eventually increases due to crack formation throughout the film. This cracking phenomenon is common to most types of thin film deposition and is the result of residual tensile stresses in the films [52-54]. Thicker films have greater residual stress and are more likely to crack. For solvent-based processes, the critical thickness for cracking is typically between 100 nm [55] and 1 μm [56]. This thickness range is for sol gel systems, but there are many similarities to

the LbL deposition of carbon black. Volume reductions that occur during drying are constrained by the underlying substrate, which leaves cracking as the only option for stress relief. Oven drying of these films enhances this effect, but also reduces sheet resistance through better densification, as will be shown in the next section.

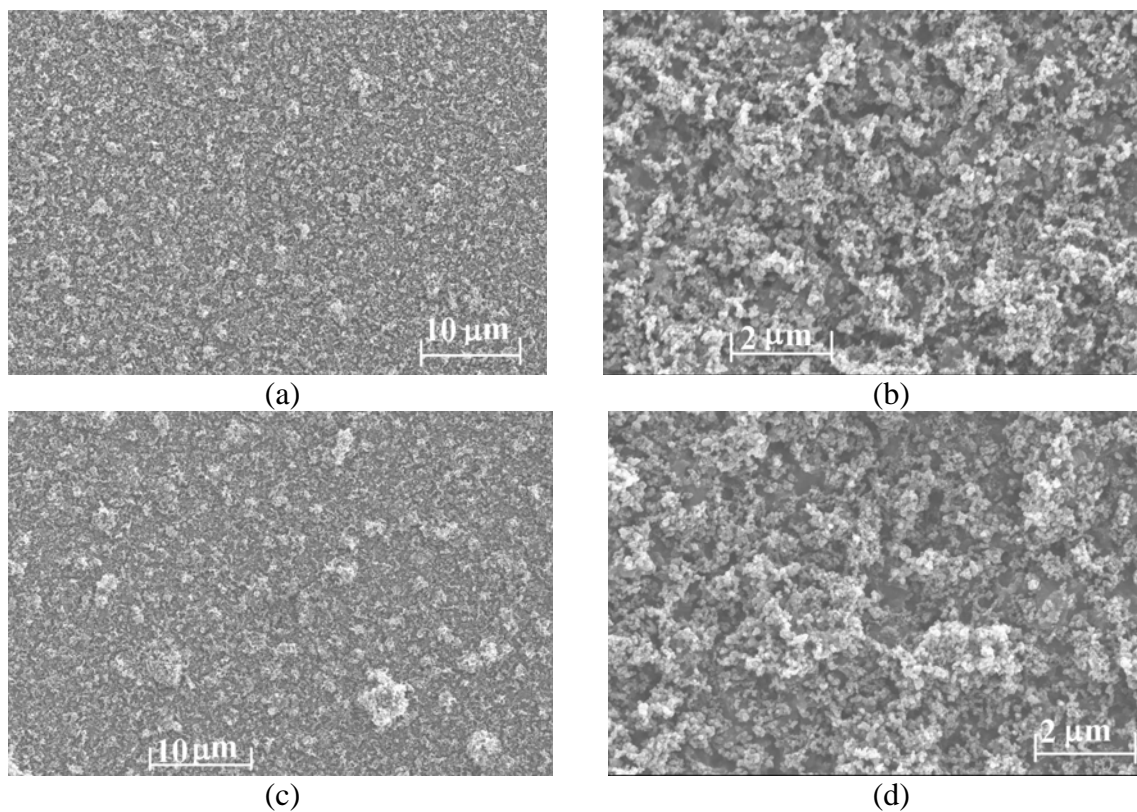


Figure 10. SEM surface images of carbon black films. 6 bilayer carbon black film without sonication at 2,000 times magnification (a) and 10,000 times magnification (b). SEM surface image of 14 bilayer carbon black film without sonication at 2,000 times magnification (c) and 10,000 times magnification (d).

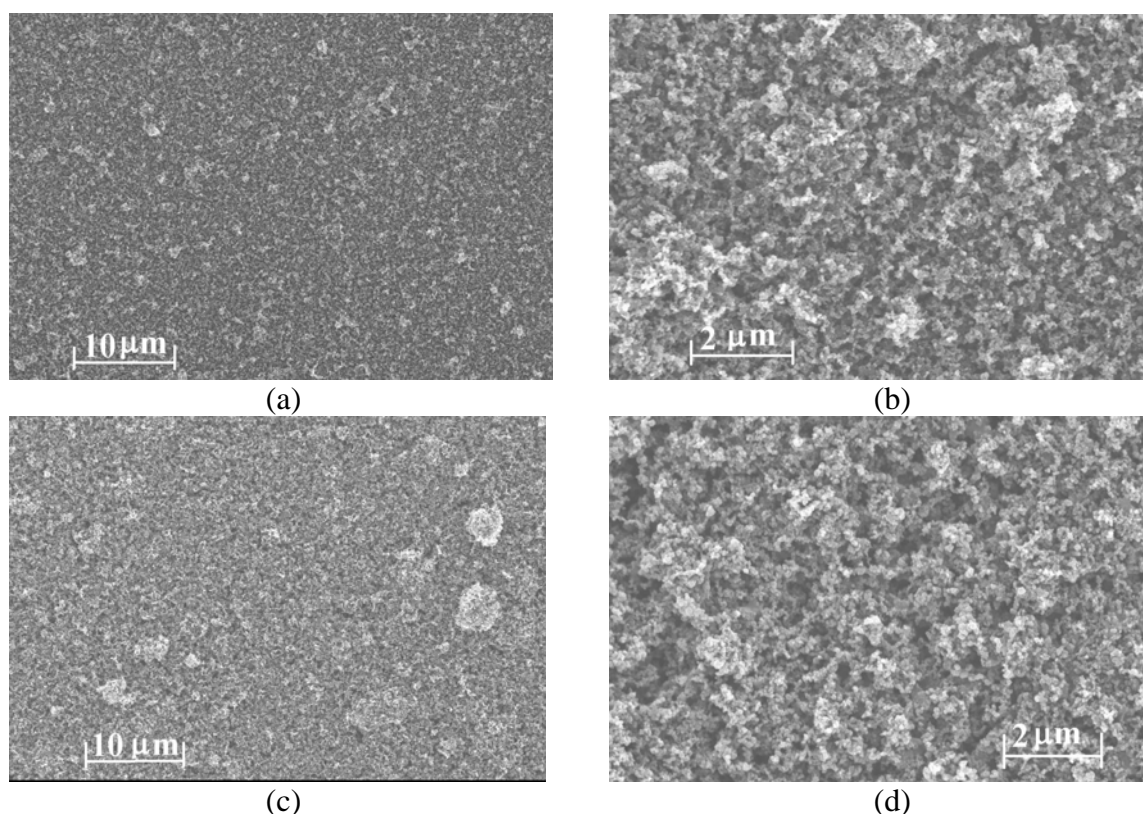


Figure 11. SEM surface images of a 6 bilayer carbon black film. Films are with sonication at 2,000 times magnification (a) and 10,000 times magnification (b). SEM surface image of a 14 bilayer carbon black film with sonication at 2,000 times magnification (c) and 10,000 times magnification (d).

Oven Effects

Figure 12 compares the sheet resistance of LbL films dried in an oven at 70°C for 15 minutes to those dried at room temperature. Films prepared from both sonicated and non-sonicated mixtures show significant improvement in electrical conductivity after oven treatment. Sonicated films achieve bulk resistivity values as low as 0.2 $\Omega\cdot\text{cm}$ following oven treatment, which is a factor of three in reduction relative to room temperature drying. Figure 13 shows the difference in bulk resistivity between sonicated films with and without oven treatment. The values for bulk resistivity are on the whole lower for oven treated films as opposed to non-oven treated films. The primary reason

for improved transport behavior in the oven treated films is further densification, as indicated by comparing film thickness as a function of the number of bilayers between identical films prepared with and without oven drying. Figure 14 shows that oven treated films are approximately 20% thinner than their non-oven treated counterparts.

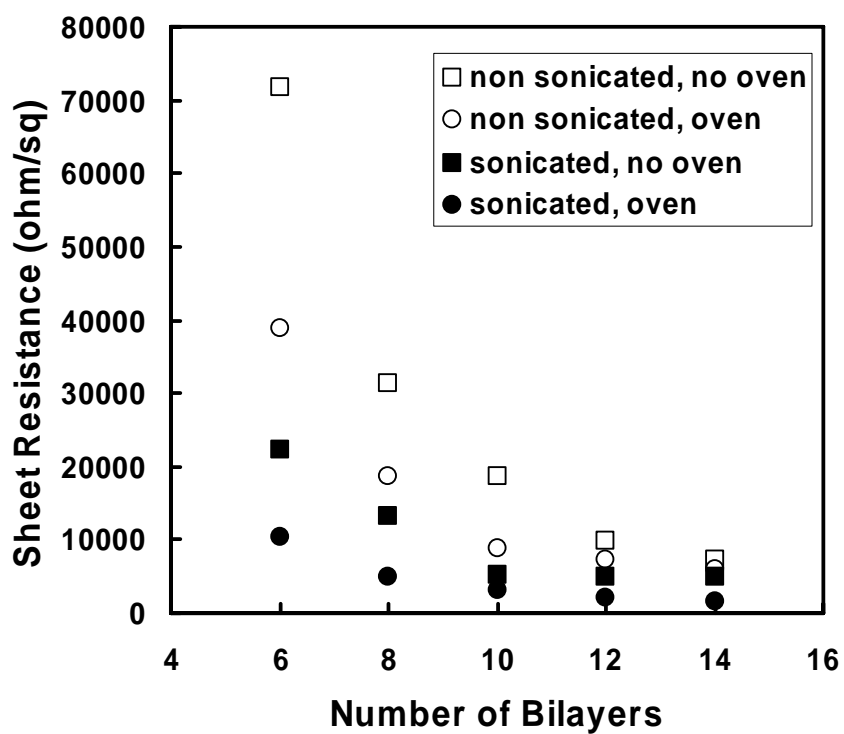


Figure 12. Sheet resistance values comparing oven treated films and room temperature dried films. The standard deviation for all values represented is less than 8%.

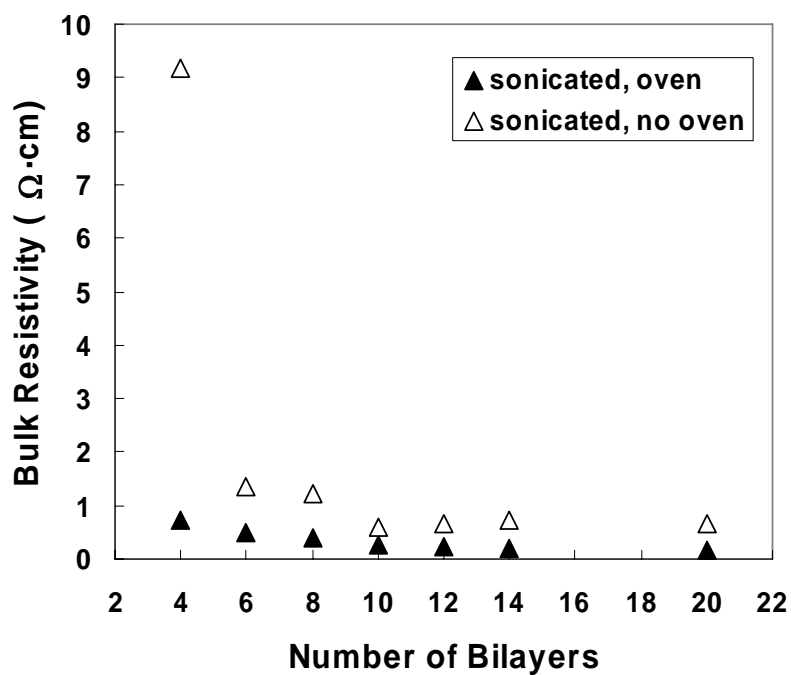


Figure 13. Bulk resistivity values comparing sonicated films with and without oven treatment.

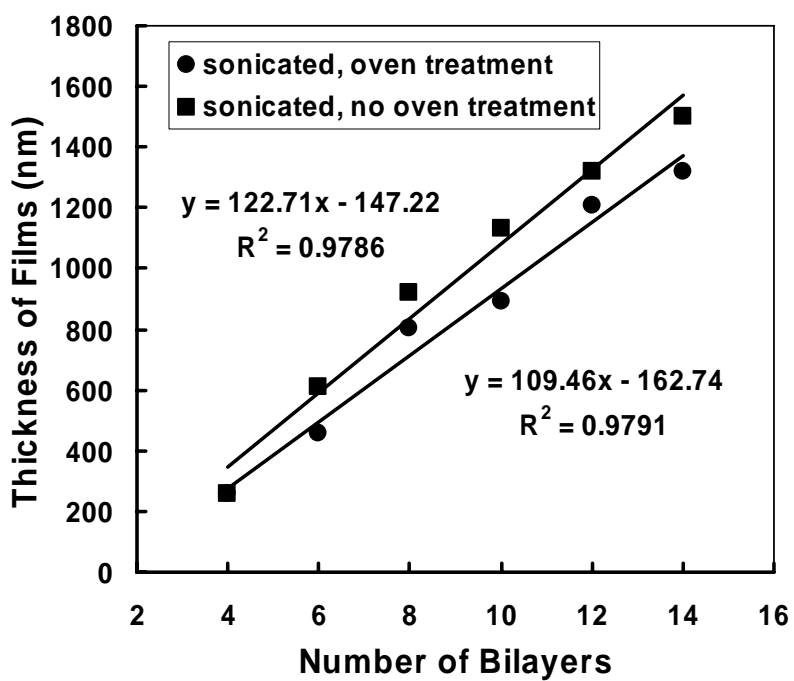


Figure 14. Film thickness values comparing sonicated films with and without oven treatment. Standard deviation of all thickness values less than 7%.

Figure 15 shows TEM images of 8-bilayer films prepared with and without oven treatment. These cross-sections provide further evidence of compaction during oven drying. Packing the same quantity of carbon black into 20% less volume generates a significant increase in contacts between particles and results in sheet resistance values that are less than half that of films dried at room temperature.

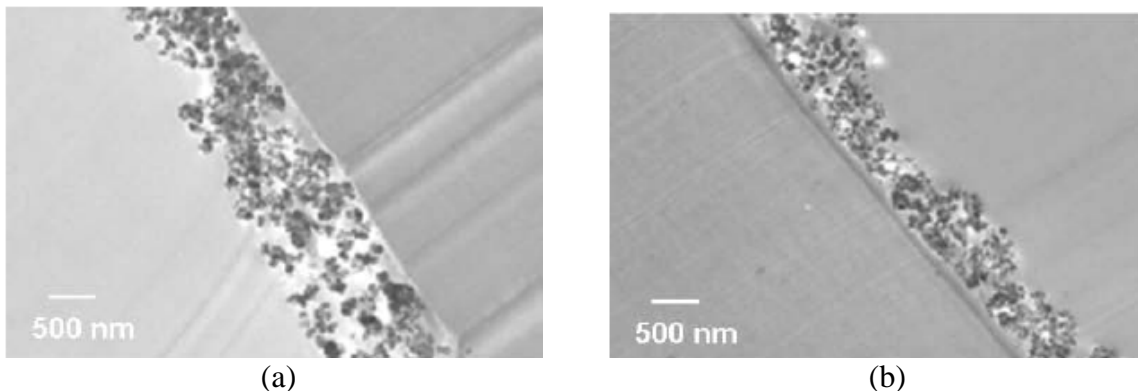


Figure 15. TEM cross-sections of 8-bilayer CB films made without (a) and with (b) oven treatment at 70°C for 15 minutes.

Table 1 shows the difference in thickness, sheet resistance, and bulk resistivity when comparing oven treated and non-oven treated films. Other drying temperatures were evaluated, as shown in Figure 16, but 70°C proved to be the best for reducing sheet resistance. Densification and compaction are working to decrease resistance, while residual stress build up and cracking result in greater sheet resistance. Cracking appears to become the dominant factor when films are dried at temperatures above 70°C.

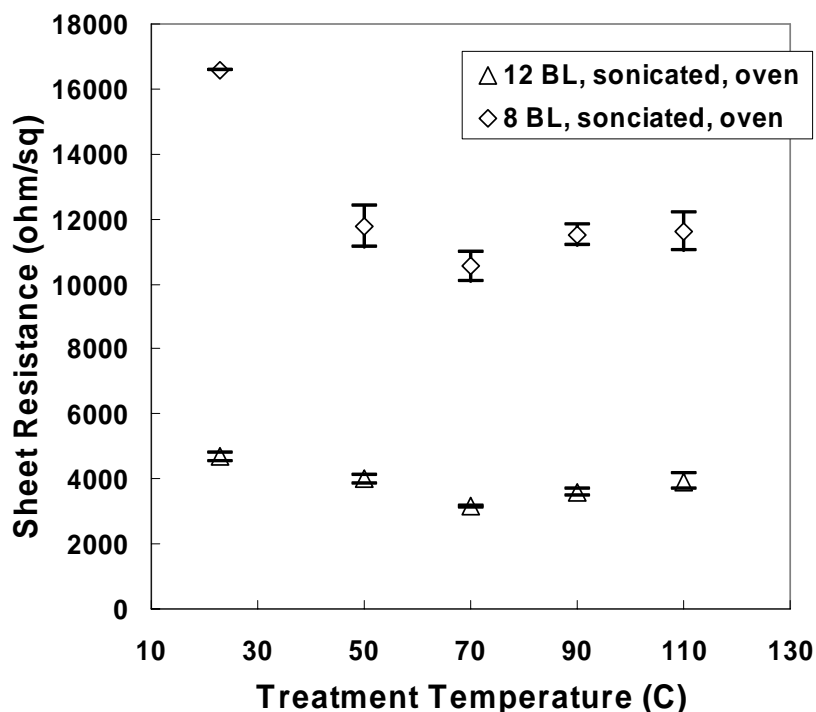


Figure 16. Sheet resistance values for sonicated films at different oven treatment temperatures with standard deviation ranges. Standard deviation bars are included to show no overlap between points.

Cracking becomes more pronounced with increasing drying temperature. Figure 17 shows the surfaces of 12-bilayer films dried at room temperature, 50, 70, and 90°C for 15 minutes. All of these films were prepared from sonicated mixtures. Significant cracks are not seen in the film dried at room temperature (Fig. 17(a)), although fine cracks may be hidden by coarse surface generated with this many bilayers. At 50°C fine cracks can be discerned (Fig. 17(b)) and in the 70 and 90°C films significant cracking is observed. The large crack seen at the center of the 90°C film (Fig. 17(d)) is nearly 1 μm wide and is down to the substrate.

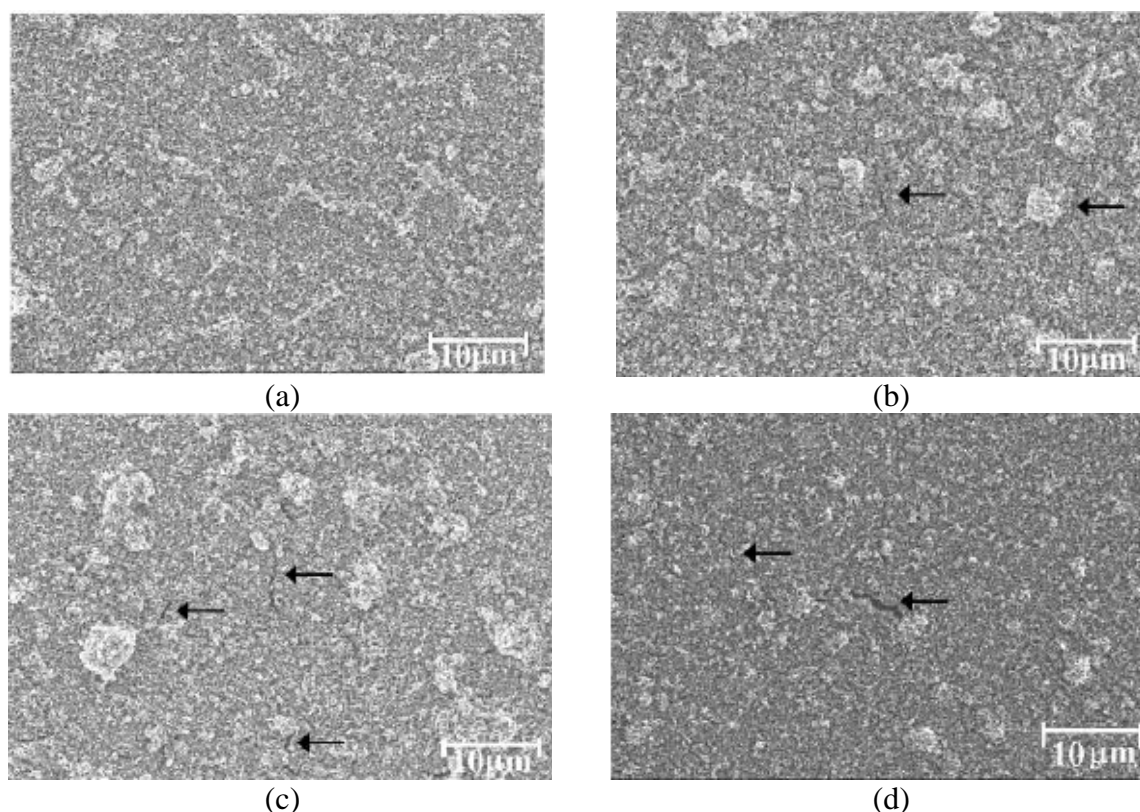


Figure 17. SEM surface images of 12-bilayer films dried at room temperature (a), 50°C (b), 70°C (c), and 90°C (d) for 15 minutes.

pH Effects

The initial pH of the carbon black mixtures stabilized with PEI and PAA are 8.4 and 3.6, respectively. When the pH of the PEI-stabilized mixture is reduced to 7 with HCl and the pH of the PAA-based mixture is raised to 5 with NaOH, the resulting films are much thinner per bilayer. Figure 18 shows how sheet resistance changes with increasing bilayers for these pH-adjusted films. Sheet resistance cannot be measured until 8-bilayers have been deposited and the values for sonicated, pH-adjusted films with oven treatment (73,000 Ω/sq) and without oven treatment (110,000 Ω/sq) are both an order of magnitude greater than a comparable film prepared without pH adjustment. The

values for sheet resistance approach values for sonicated films without oven treatment at around 14 bilayers, but sheet resistance remains higher for pH adjusted films.

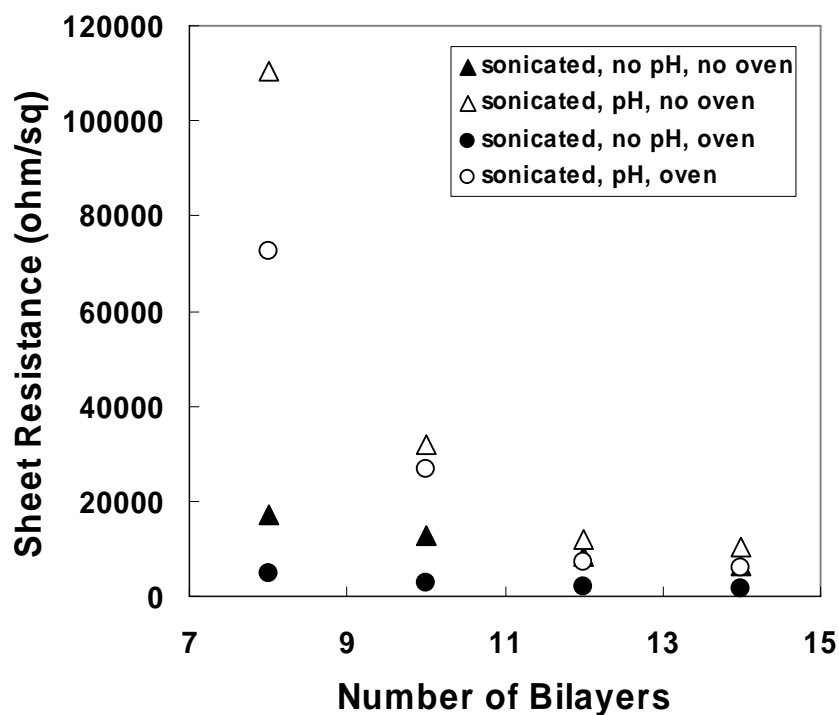


Figure 18. Comparison of sheet resistance values for pH treated films and films without pH treatment. Standard deviation for all values less than 10%.

Unlike with oven treatment and sonication, film thickness is the primary reason for this reduced electrical conductivity in films made from pH-treated mixtures. Without pH adjustment, films grow by approximately 100 nm per bilayer, but the growth rate is only about 50 nm per bilayer for pH-adjusted films. Figure 19 shows the large difference in film thickness between pH-adjusted films and films that have not been pH-adjusted. Decreasing the pH of PEI and increasing the pH of PAA lead to increased charge density for both of these weak polyelectrolytes [57,58]. It is already well-

established that layer thickness decreases with increasing charge density due to fewer loops in the polymer chains and greater electrostatic bonding [58-60]. Figure 20 shows the difference in bulk resistivity between pH adjusted and non-adjusted films.

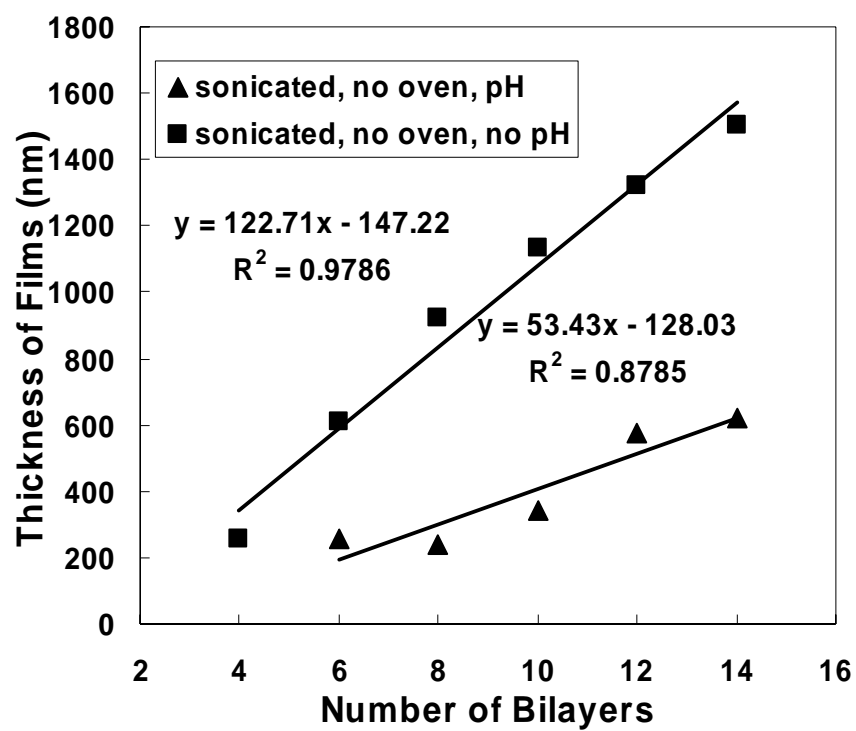


Figure 19. Thickness comparison between series of pH treated films and non-pH treated films. Standard deviation of all thickness values less than 15%.

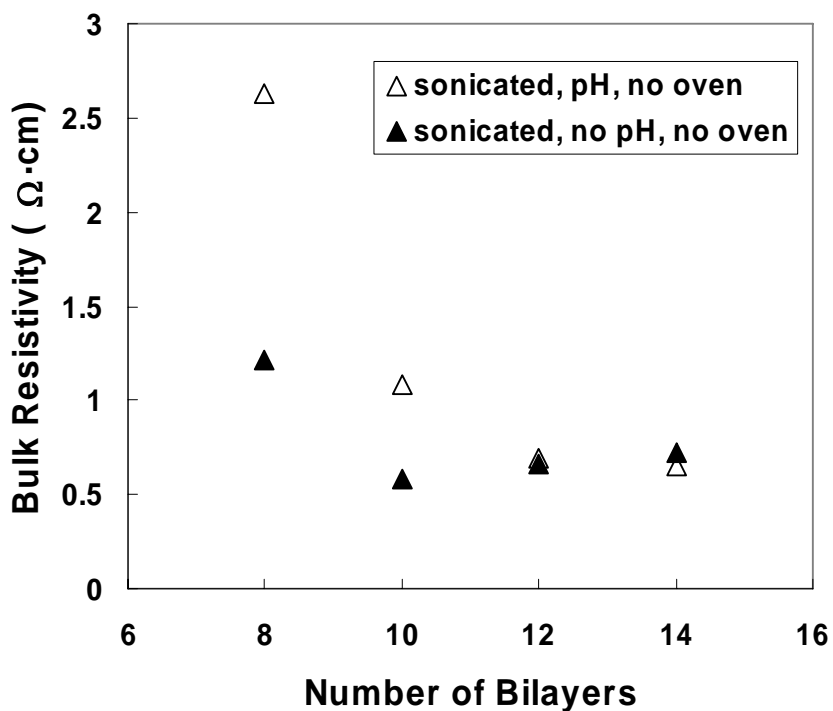


Figure 20. Bulk resistivity values comparing sonicated, non-oven treated films with and without pH adjustment.

The effects of oven treatment on pH-adjusted films are consistent with that shown previously. With oven treatment, the sheet resistance values for pH-adjusted films were less than pH-adjusted films that were not subjected to oven treatment. This trend is easily seen above in Figure 18. Another effect of oven treatment is that film thickness is reduced with oven treatment. This occurrence is observed in sonicated films, with oven treatment the films are roughly 20% thinner than films that have not been oven treated. A similar correlation can be noted with oven treatment of pH-adjusted films, as shown in Figure 21.

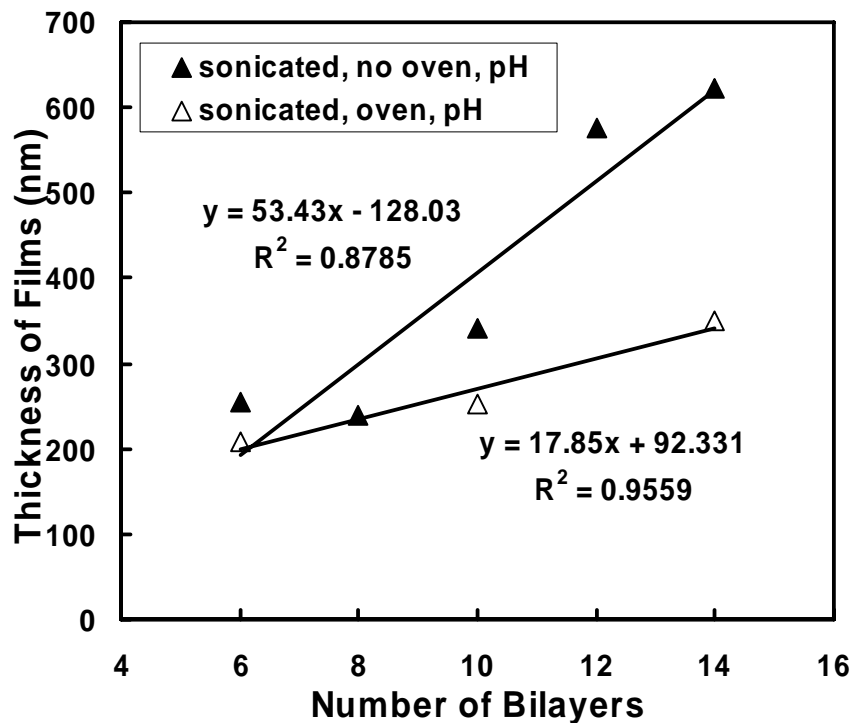


Figure 21. Film thickness values comparison between sonicated, pH-adjusted films with and without oven treatment. Standard deviation of thickness values less than 15%.

Table 1 above shows the difference in values in sheet resistance, thickness, and bulk resistivity comparing pH-adjusted films and non-adjusted films. It can be seen that once sheet resistance measurements can be made on pH-adjusted films, the bulk resistivity is very similar to films that are not pH-adjusted. This shows a correlation between film thickness and sheet resistance values for this set of carbon black thin films. As shown in Table 1, all variations in processing ultimately converge due to film thickness. Significant changes in overall film composition are not produced using these variables.

The reduced thickness in films made from pH-adjusted mixtures results in relatively transparent films, as shown in Figure 22. It should be noted that the substrate

contains a given number of bilayers on both sides of a transparent PET film, so percent transmission (%T) values would be even greater if only one side were coated. For example, the 4-bilayer film in Figure 23 would have a visible light transmission of approximately 83% if only one side of the PET had been coated.

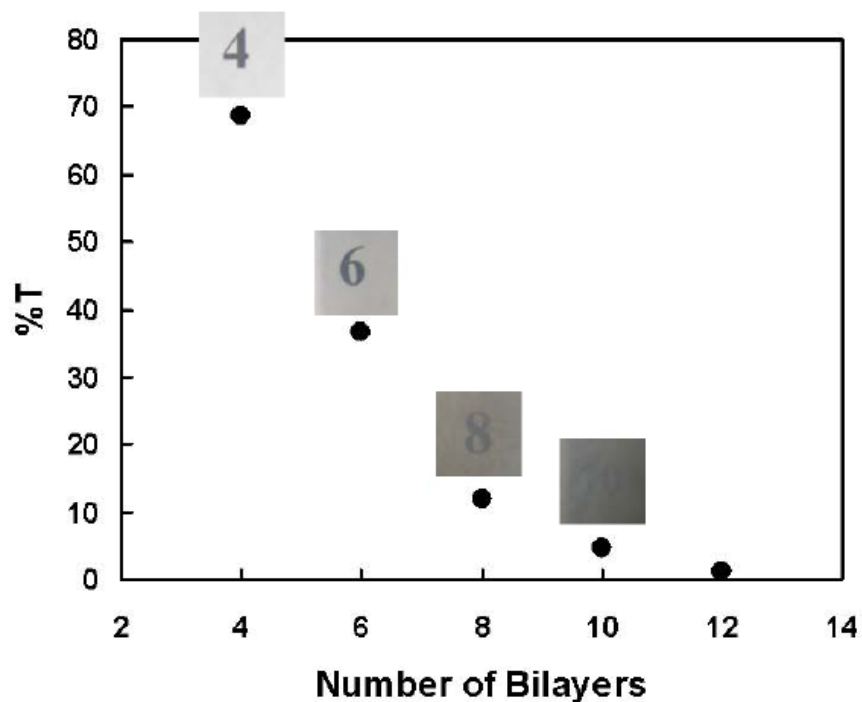


Figure 22. Optical transparency from pH treated films along with values for percent transmission.

Surface images shown in Figure 23 look very similar to non-adjusted films at low magnification (Fig. 23(a) and (c)), but patchy surface coverage that allows the underlying substrate to be seen is revealed in 6-bilayer film at higher magnification (Fig. 23(b)). These micron-sized holes in the film reduce electrical conductivity and enhance optical transparency. At 14-bilayers the film has achieved complete coverage of the substrate (Fig. 14(d)) and does not show the types of cracks observed in films made

without pH-adjustment. Transparent carbon black thin films may be useful for low cost electrostatic dissipation in display applications or for light filtration.

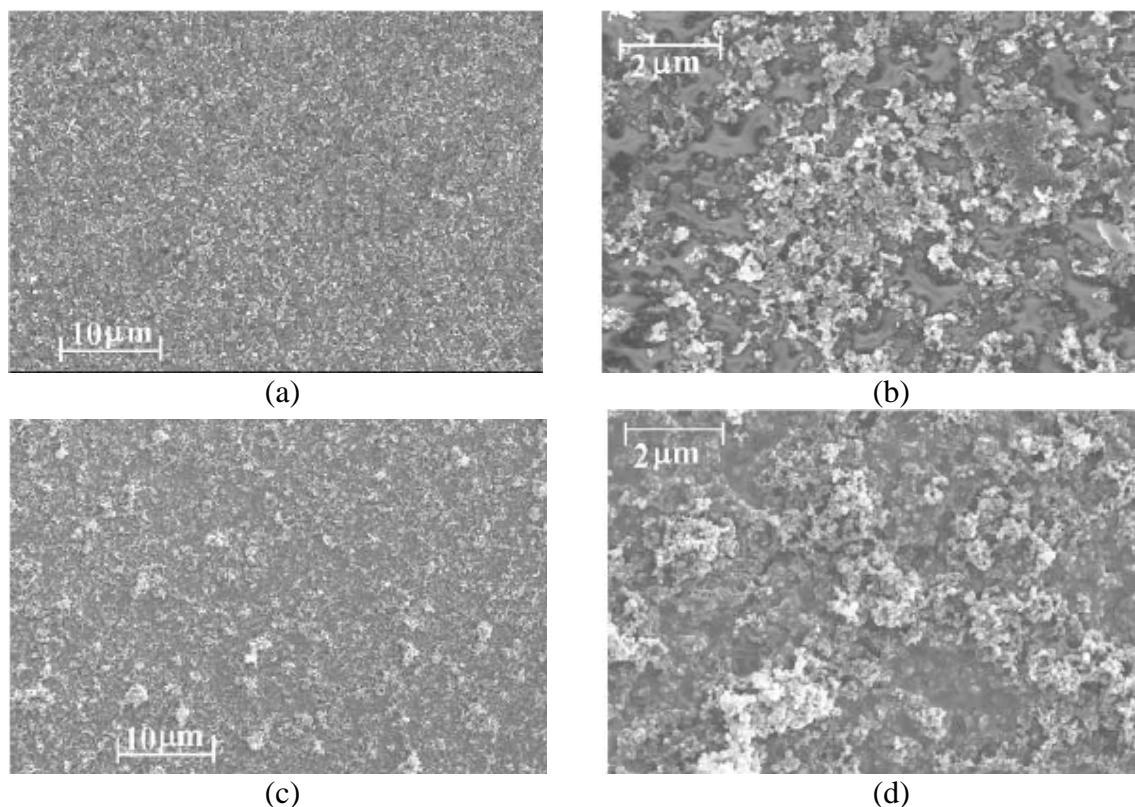


Figure 23. SEM surface images of a 6-bilayer carbon black film, prepared from pH-adjusted mixtures, show a relatively smooth surface at low magnification (a), but the underlying substrate can be seen at higher magnification (b). Surface images of a 14-bilayer film show no evidence of cracking at low magnification (c) and full coverage of the substrate at high magnification (d).

Conclusions

Highly conductive carbon black-filled polymer composite thin films were prepared using LbL assembly. The lowest sheet resistance values are obtained when polymer-stabilized, aqueous carbon black mixtures are sonicated prior to deposition and films are oven treated at 70°C after deposition. Cracking in these thin films was typically observed when more than 10 bilayers were deposited due to residual stress

generated during drying. Optically transparent films were produced by altering the pH of deposition mixtures, which resulted in thinner bilayers due to increased charge density on the stabilizing polyelectrolytes. This increased transparency is coupled with increased sheet resistance that is also associated with reduced film thickness and poor surface coverage. Further reductions in sheet resistance through compositional changes in the deposition mixtures are discussed in Chapter III. Changes in the carbon black-polymer ratio result in compositional variation in the deposited bilayers. These changes are expected to change the number of bilayers at which cracking becomes a significant problem. Depositing layers containing no carbon black with carbon black-filled layers also produce beneficial results.

CHAPTER III

COMPOSITIONAL VARIABLES

In Chapter II, processing variables were manipulated while keeping carbon black and polymer concentrations fixed in the deposition mixtures. Chapter III builds upon the results from Chapter II by making use of the processing parameters that produced the lowest sheet resistance. These optimized processing variables included, sonication of mixtures for 15 minutes prior to film deposition, no pH-adjustment of the mixtures prior to deposition, and oven drying for 15 minutes at 70°C immediately following film deposition. In Chapter III, keeping these conditions fixed, compositional changes are evaluated that include changing the polymer concentration in the deposition mixtures, purposely leaving carbon black absent from a particular deposition solution, altering the polymer concentration between the solutions, (i.e., having polyethylenimine (PEI) be at 0.1wt% while poly(acrylic acid) (PAA) being at 0.05wt%), and changing the ionic strength of the mixtures by adding specific molar amounts of NaCl.

Materials and methods used in this study are identical to those outlined in Chapter II. When NaCl was added to a deposition mixture, it was added following the carbon black addition and after the carbon black-polymer mixture had reached equilibrium, sonication was then performed.

Results and Discussion

In Chapter II, it was shown that sonication of carbon black-polyelectrolyte mixtures prior to film deposition resulted in lower values of sheet resistance. It was also

shown that oven treatment at 70°C further decreases the value of thin film sheet resistance. Combining these optimal processing conditions with variations in deposition mixture composition, yields further improvements in transport behavior. Four compositional variables are evaluated below: (1) different carbon black concentration to polymer concentration ratios, (2) different polymer concentration between positively and negatively charged solutions, (3) intentionally leaving carbon black absent from one polymer solution or the other, and (4) using NaCl to modify the ionic strength of the deposition mixtures prior to deposition.

Polymer Ratio Variation

In Chapter II, the standard deposition mixture recipe was 0.25wt% carbon black mixed in 0.05wt% PEI and PAA solutions. When changing the polymer concentration from 0.025-0.5wt%, the amount of carbon black was held constant at 0.25wt%. Figure 24 shows the change in sheet resistance for each polymer concentration for 8 and 14 bilayer films. For both sets of bilayers, the films made with 0.25wt% carbon black in 0.1wt% PEI and PAA exhibited the lowest sheet resistance values. One possible explanation for this behavior is that there should be a point where the concentration of polymer is just enough to stabilize all of the carbon black in the mixtures without any excess. Too little polymer produces a weak, defective film, while too much polymer creates separation between carbon black particles. This optimal concentration was used to produce a full series from 6 to 14 bilayers, and the results show that this series has lower sheet resistance values relative to the best series from Chapter II, as shown in Figure 25. As noted in previous experiments, the sheet resistance tends to taper off at

higher bilayers due to submicron cracking in the films starting between 10 and 12 bilayers.

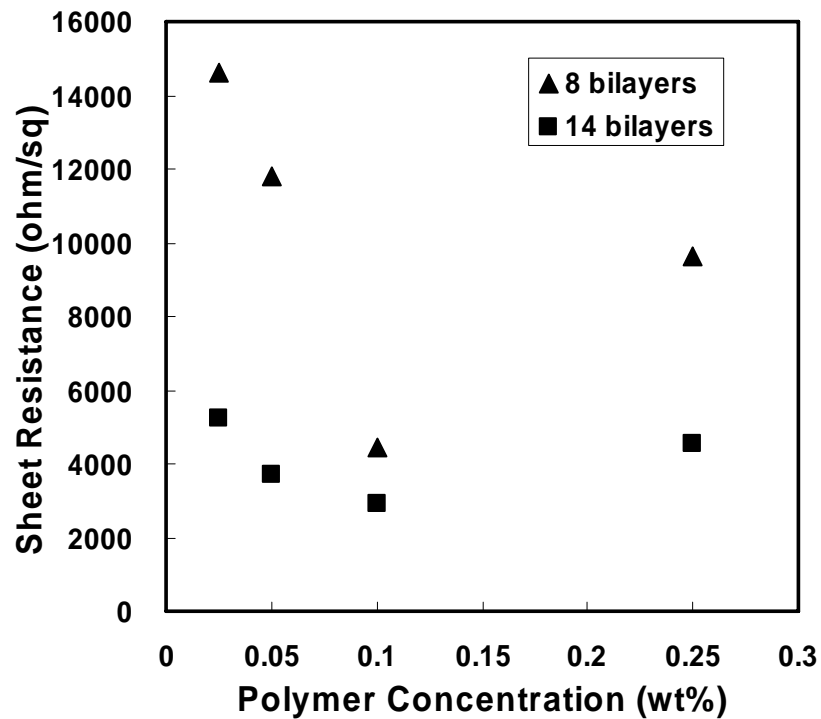


Figure 24. Comparison of sheet resistance values for different polymer concentrations. Standard deviation for 0.25wt% polymer at 8 bilayers is 14%, all other standard deviations are less than 6%.

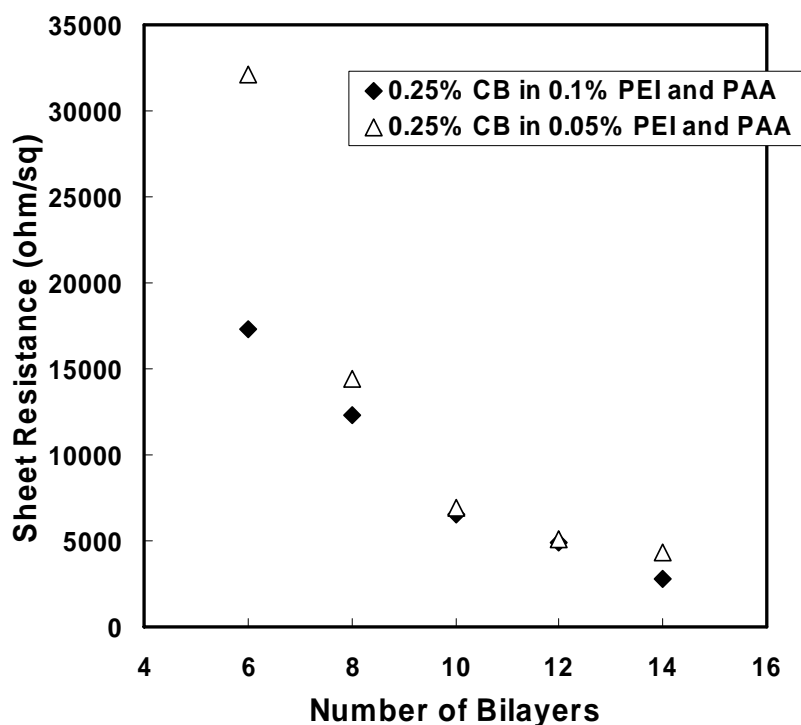


Figure 25. Comparison of sheet resistance values between a series of films generated from aqueous mixtures of 0.25wt% CB in 0.1wt% PEI and PAA and 0.25wt% CB in 0.05wt% PEI and PAA. Standard deviation for 0.05wt% PEI and PAA at 6 bilayers is 12%, the rest of the values have standard deviation less than 8%.

The thickness of these two series as a function of bilayers deposited is shown in Figure 26. The growth rate per bilayer of the new series (~165 nm per bilayer) is much greater than the growth of the original series (~140 nm per bilayer), which largely accounts for the lower sheet resistance values observed. The mixtures with 0.1wt% PEI and PAA are further from neutral than the mixtures with 0.05wt% polymer which produces lower charge density and thicker deposition as a result. Charge density decreases as the pH of PEI is increased and PAA is decreased. Reduced charge density causes these polyelectrolytes to assume a more coiled conformation and there is less repulsion between polymer chains, resulting in thicker deposition [57-60].

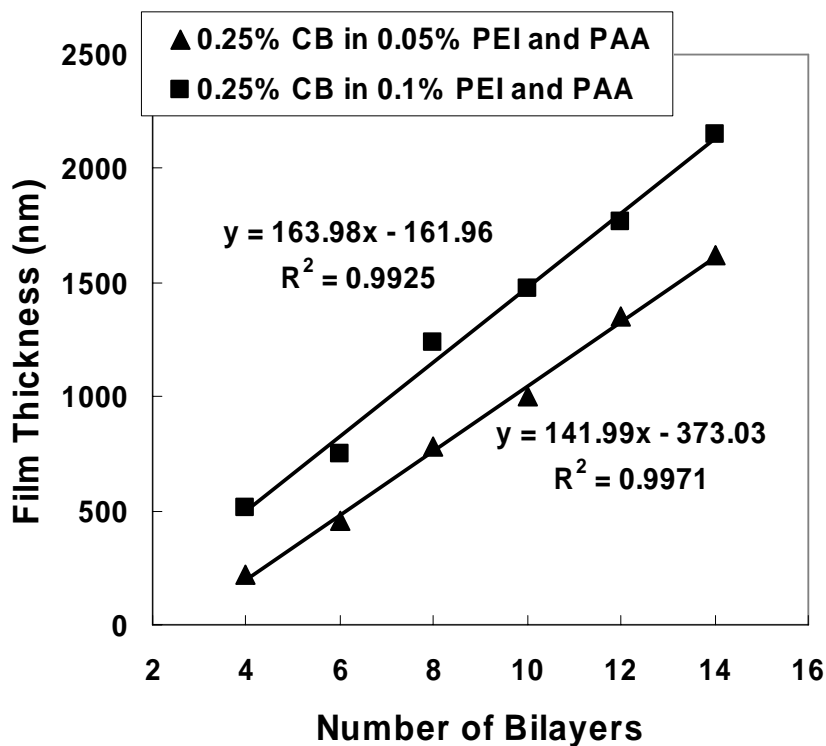


Figure 26. Thickness comparison of films, one series being 0.25wt% CB in 0.1wt% PEI and PAA, the second series being 0.25wt% CB in 0.05wt% PEI and PAA. Standard deviation for thickness values below 8%.

From these thickness and sheet resistance measurements, bulk resistivity of the films was calculated. Table 2 shows the data between the original optimal series and the newly found optimal series. Bulk resistivity values are very similar, which suggest that thin film composition and connectivity is similar. Changing composition of the deposition mixtures simply allows a relatively thick film to be made with fewer bilayers.

Table 2

Thickness, sheet resistance, bulk resistivity, and pH levels for five different sets of films with different compositions.

0.25% CB in 0.05% PEI and PAA, sonicated, no pH adjustment, oven dried						
pH Levels		Bilayers	Thickness (nm)	Sheet Resistance (Ω/sq)	Bulk Resistivity (Ω·cm)	
PEI	PAA	4	218.78	521351.84	11.41	
		6	455.00	32116.89	1.46	
8.47	3.72	8	778.63	14469.19	1.13	
		10	1000.67	6918.87	0.69	
		12	1352.70	5080.31	0.69	
		14	1623.65	4288.73	0.69	
0.25 % CB in 0.1% PEI and PAA, sonicated, no pH treatment, oven dried						
pH Levels		Bilayers	Thickness (nm)	Sheet Resistance (Ω/sq)	Bulk Resistivity (Ω·cm)	
PEI	PAA	4	510.09	334396.21	17.06	
		6	750.41	17346.24	1.30	
9.00	3.55	8	1234.73	12324.63	1.52	
		10	1472.84	6585.11	0.97	
		12	1767.15	4857.69	0.86	
		14	2148.21	2816.42	0.61	
0.25% CB in 0.1% PEI and 0.05% PAA, sonicated, no pH treatment, oven dried						
pH Levels		Bilayers	Thickness (nm)	Sheet Resistance (Ω/sq)	Bulk Resistivity (Ω·cm)	
PEI	PAA	4	685.14	13849.31	0.95	
		6	1327.98	3196.69	0.42	
9.00	3.72	8	2014.63	1799.15	0.36	
		10	2952.60	900.20	0.27	
		12	3457.99	806.38	0.28	
		14	4247.90	558.98	0.24	
0.25% CB in 0.05% PAA and plain 0.05% PEI, sonicated, no pH treatment, oven dried						
pH Levels		Bilayers	Thickness (nm)	Sheet Resistance (Ω/sq)	Bulk Resistivity (Ω·cm)	
PEI	PAA	4	621.76	17599.75	1.09	
		6	1428.39	4424.54	0.63	
9.22	3.72	8	2022.16	2582.29	0.52	
		10	2476.65	991.00	0.25	
		12	N/A	779.21	N/A	

Table 2
Continued.

0.25% CB in 0.05% PAA and plain 0.1% PEI, sonicated, no pH treatment, oven dried					
pH Levels		Bilayers	Thickness (nm)	Sheet Resistance (Ω/sq)	Bulk Resistivity ($\Omega\cdot\text{cm}$)
PEI	PAA	4	995.67	5501.60	0.55
		6	2210.55	1475.13	0.33
9.44	3.72	8	3358.26	872.56	0.29
		10	5426.91	504.82	0.27
		12	6870.37	415.74	0.29
		14	8069.58	327.87	0.26

* The standard deviation for all values within this table is less than 8%.

Surface images of films from both series are shown in Figure 27. These SEM images do not reveal significant micro-structural differences between the films made with these two polymer concentrations. At higher bilayers (Fig. 27 (c) and (d)), cracking is observed in both films and seems to be the primary cause for the tapering off of sheet resistance values beyond 10 bilayers (Fig. 25). The cracks observed in the film made with 0.1wt% polymer (Fig. 27(d)) appear wider due to the greater thickness achieved at 12 bilayers.

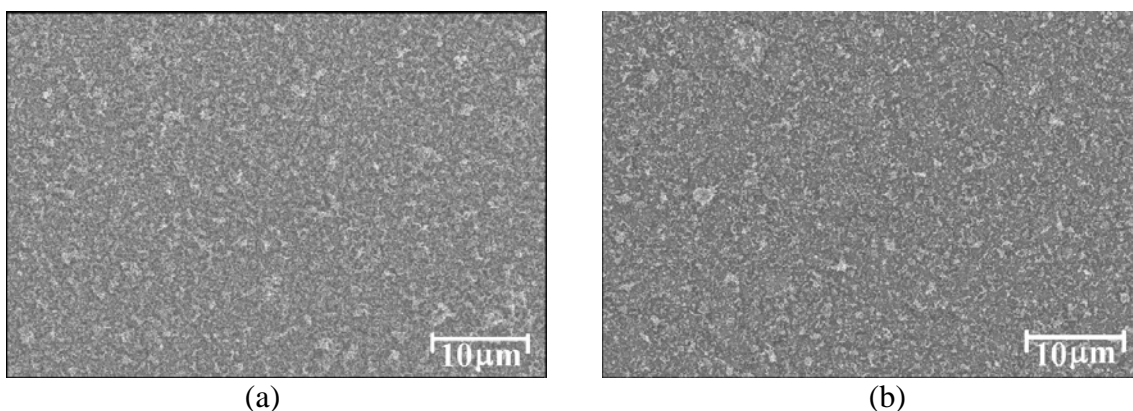


Figure 27. SEM surface images of 6 BL films made with 0.25% CB in 0.05% PEI and PAA (a), 0.25% CB in 0.1% PEI and PAA (b), 12 BL film made with 0.25% CB in 0.05% PEI and PAA (c), and 14 BL film made with 0.25% CB in 0.1% PEI and PAA (d).

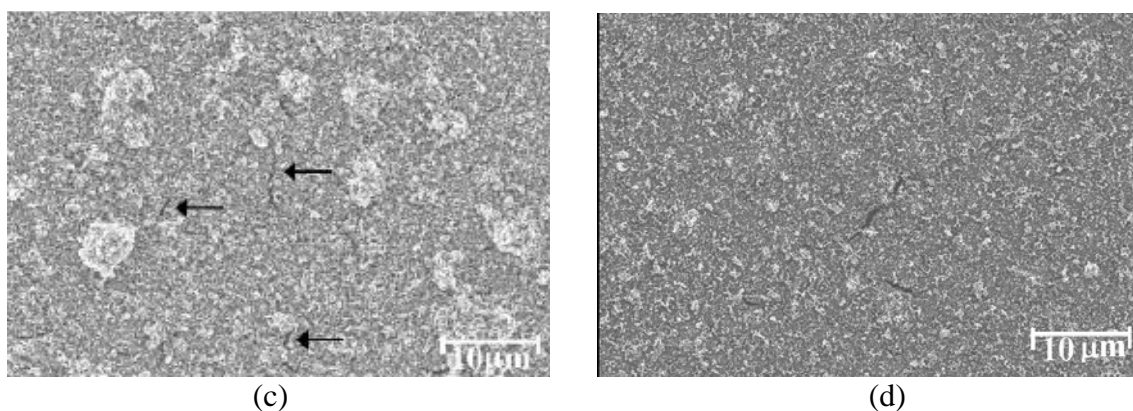


Figure 27. Continued.

Mismatched Concentration of Polyelectrolytes

Following the discovery that increasing the polymer concentration to 0.1wt% in solution gave faster reduction of sheet resistance, PEI and PAA were varied between 0.05wt% and 0.1wt%. Figure 28 shows the sheet resistance results for films made with 0.25wt% carbon black in 0.05wt% PAA and 0.1wt% PEI. This series gave sheet resistance values an order of magnitude lower than the previous two series at every bilayer tested.

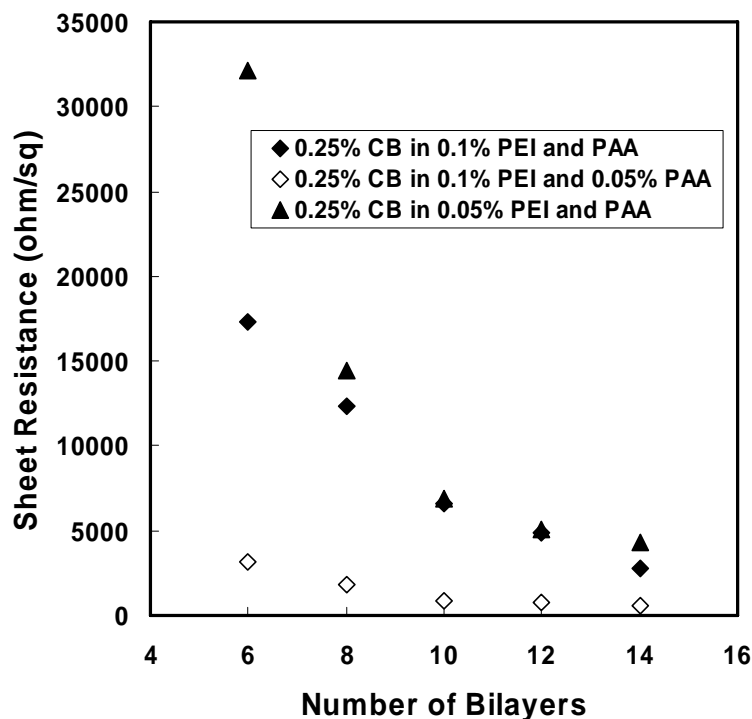


Figure 28. Sheet resistance values comparing films made with 0.25wt% CB in 0.05wt% PEI and PAA, 0.25wt% CB in 0.1wt% PEI and PAA, and 0.25wt% CB in 0.05wt% PAA and 0.1wt% PEI. Standard deviation for 0.05wt% PEI and PAA at 6 bilayers is 12%, the rest of the values have standard deviation less than 8%.

SEM surface images shown in Figure 29 are very uniform looking, but have a more granular appearance than previous series (Fig. 27). These results suggest that PAA is in excess at 0.1wt% and may be obscuring the observed microstructures in Figure 30. Another explanation is that this specific combination of mixtures induces carbon black aggregation during deposition. This may explain the dramatic increase in growth rate shown in Figure 30. The problem of cracking still persists at higher bilayers and the cracks are more evident because of the increased thickness of these films (Fig. 29(b)). The mismatched films grew at a rate of ~ 325 nm per bilayer, which is twice the rate of the 0.1wt% in both PEI and PAA series.

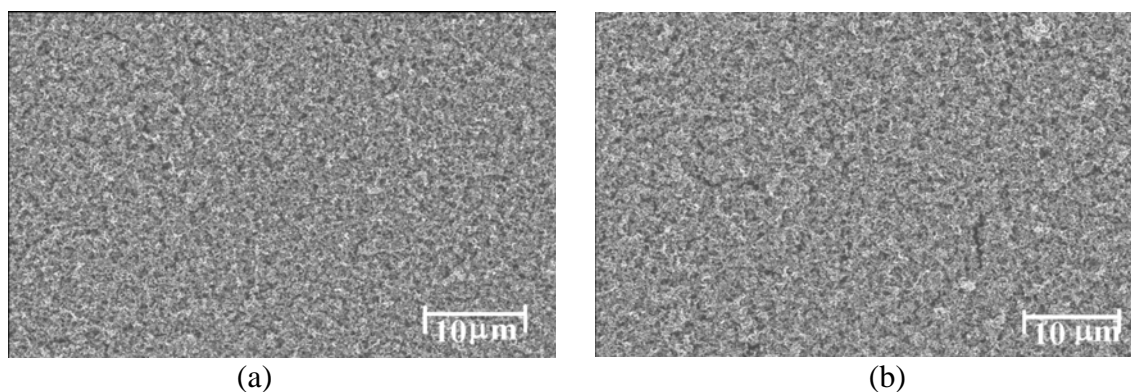


Figure 29. SEM surface images of 6 BL films made with 0.25% CB in 0.25% CB in 0.1% PEI and 0.05% PAA (a). Also, 14 BL film made with 0.25% CB in 0.1% PEI and 0.05% PAA (b).

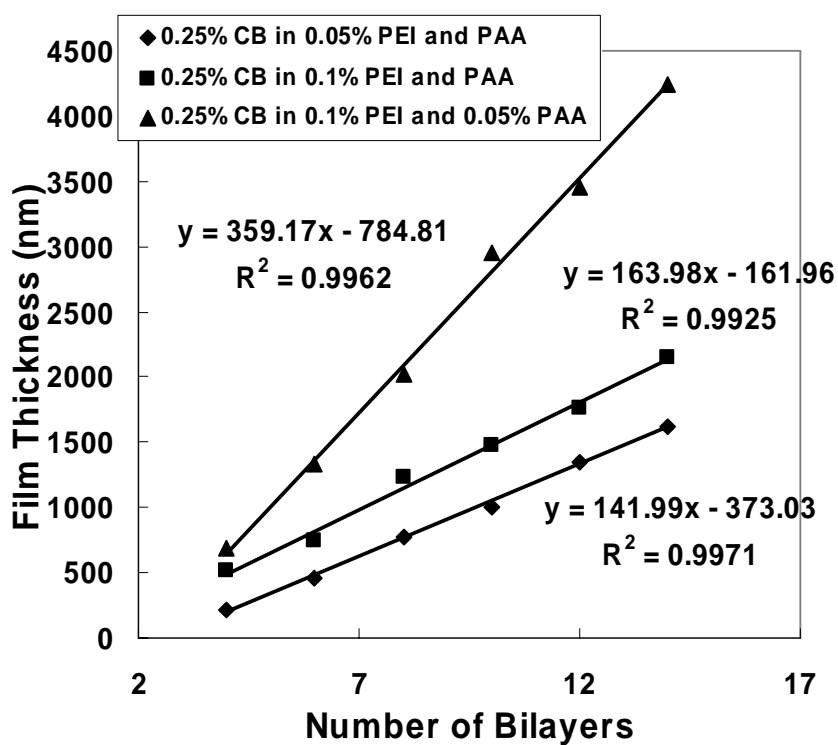


Figure 30. Thickness comparison of films, one series being 0.25% CB in 0.05% PEI and PAA, one series being 0.25%CB in 0.1% PEI and PAA, and the final series being 0.25% CB in 0.1% PEI and 0.05% PAA. Standard deviation for thickness values less than 10%.

Despite being much thicker than their concentration-matched counterparts, this series of films has lower bulk resistivity values. This reduction in sheet resistance values

can be attributed to the fact that the concentration of carbon black in these films increased to 48wt%, which is an increase of 3wt% compared to the series generated with a polymer concentration of 0.05wt%.

Intentional Absence of Carbon Black in Mixtures

Intentionally leaving carbon black out of the PEI or PAA mixture is yet another way to tailor deposition. The best recipe from the previous section was used as the starting point, but carbon black was left out of PEI for one series, and left out of PAA for a second series. Sheet resistance values for these new series were then compared to those with carbon black in both PEI and PAA. When carbon black was left out of PEI, the sheet resistance values were an order of magnitude lower for all bilayers (~800 Ω /sq at 14 bilayers) than either the standard series or when carbon black was left out of PAA. When carbon black was left out of PAA, the values for sheet resistance were similar to those of the standard series. Figure 31 illustrates the difference in sheet resistance values between these three series.

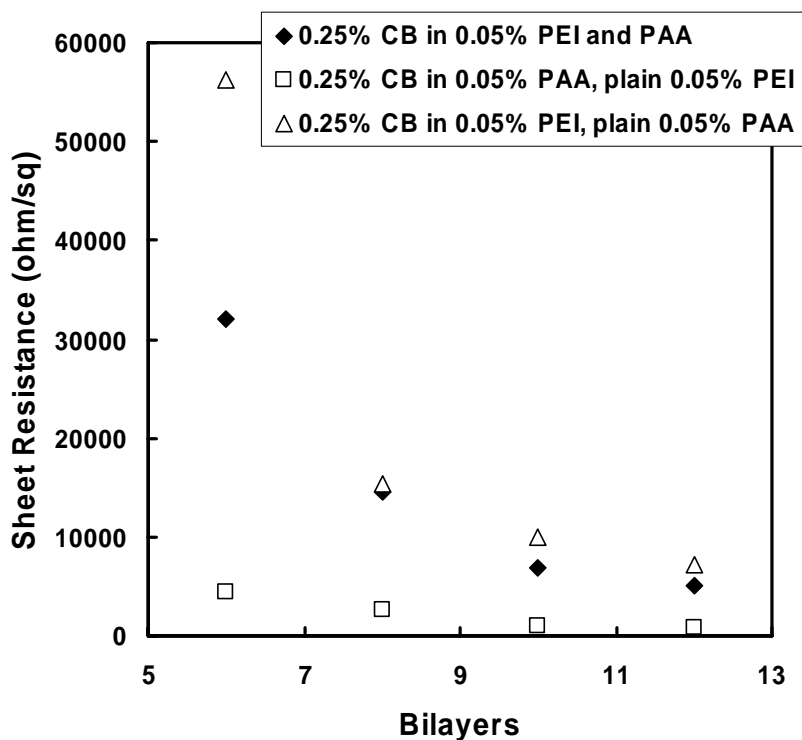


Figure 31. Comparison of sheet resistance values between the original recipe and intentionally leaving carbon black out of either PEI or PAA in mixture. Standard deviation for 0.25wt% CB in 0.05wt% PEI and PAA at 6 bilayers is 12%, the rest of the values have standard deviation less than 8%.

Figure 32 shows the SEM surface images taken of the new series to compare the film uniformity and packing of particles on the surface. All of the films appear uniform and exhibit the same cracking phenomenon as other films at higher bilayers. The original recipe films (Fig. 27 (c)) and the films where carbon black was absent from PAA have similar values for sheet resistance, and have a similar deposition quality when comparing images. The films composed of mixtures where carbon black was absent from PEI result in a very uniform deposition and the carbon black particles are very well packed together and in close contact.

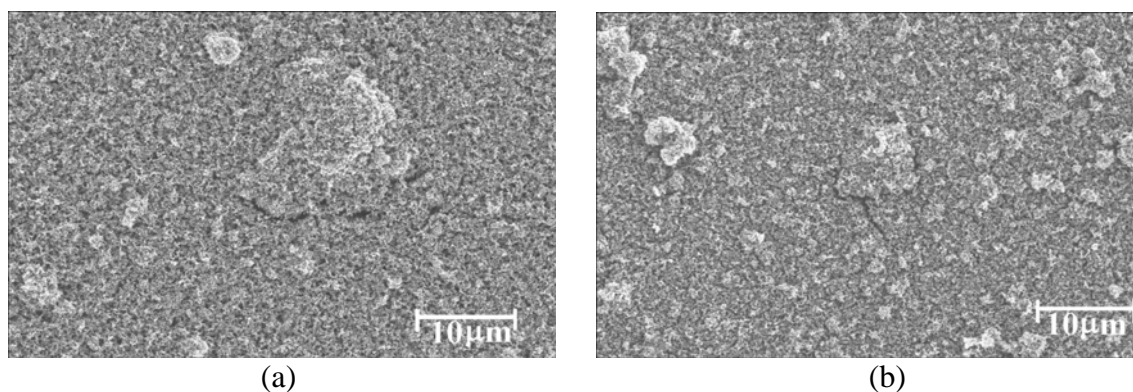


Figure 32. SEM surface images of 12 bilayer films of 0.25wt% CB in 0.05wt% PEI and PAA. Carbon black left out of PEI (a), and carbon black left out of PAA (b).

Unlike PEI, PAA is a rigid polymer at room temperature, with a glass transition temperature of 100°C [61,62], so it is unable to completely envelope the carbon black particles (allowing them to make better contact and increase conductivity). It is likely that the much lower glass transition temperature of PEI more effectively wets the carbon black particles, creating an insulating sheath. When carbon black is left out of the PEI solution it can more effectively interdiffuse with the carbon black-filled PAA layers, minimizing the insulating effects [63,64].

Polymer Variation with Carbon Black absent from PEI

When leaving carbon black absent from PEI, the sheet resistance values were lower than when carbon black was in both PEI and PAA and when carbon black was left out of PAA. Figure 33 shows surface images of these most recent films. SEM surface images show the deposition to be more uniform (Fig. 33(b)) than previous series (Fig. 27, Fig. 29, and Fig. 32) and particles are in close contact with each other, but cracking is much worse at higher bilayers. Mixing and matching polymer ratios while intentionally leaving carbon black out of PEI solutions results in still further improvement in these

films, as seen in Figure 34. When films were generated with 0.25wt% carbon black in 0.05wt% PAA with plain 0.1wt% PEI, the sheet resistance values were reduced to $\sim 325 \Omega/\text{sq}$ at 14 bilayers. Thickness measurements for this low sheet resistance series showed that thicker films have lower sheet resistance values. Figure 35 illustrates the thickness comparison of these films to previous films. These films grew at a rate of $\sim 730 \text{ nm}$ per bilayer; this is twice the growth rate of the next largest growth rate. This explains the heavy cracking in these films. In all of the series, at a thickness around 1500 nm , cracking appears. Ultimately, achieving greater thickness per bilayer will give the greatest reduction in sheet resistance per bilayer. The concentration of carbon black remains relatively unchanged (48-50wt%), leaving thickness the key parameter for controlling sheet resistance.

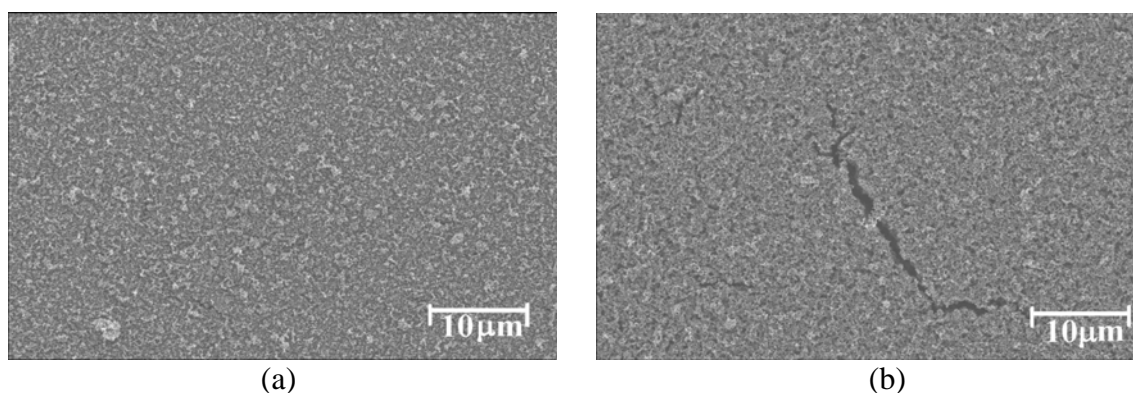


Figure 33. SEM surface images of mismatched films. A 12 bilayer film with 0.25% CB in 0.1% PAA and plain 0.1% PEI (a), and a 14 bilayer film with 0.25% CB in 0.05% PAA and plain 0.1% PEI (b).

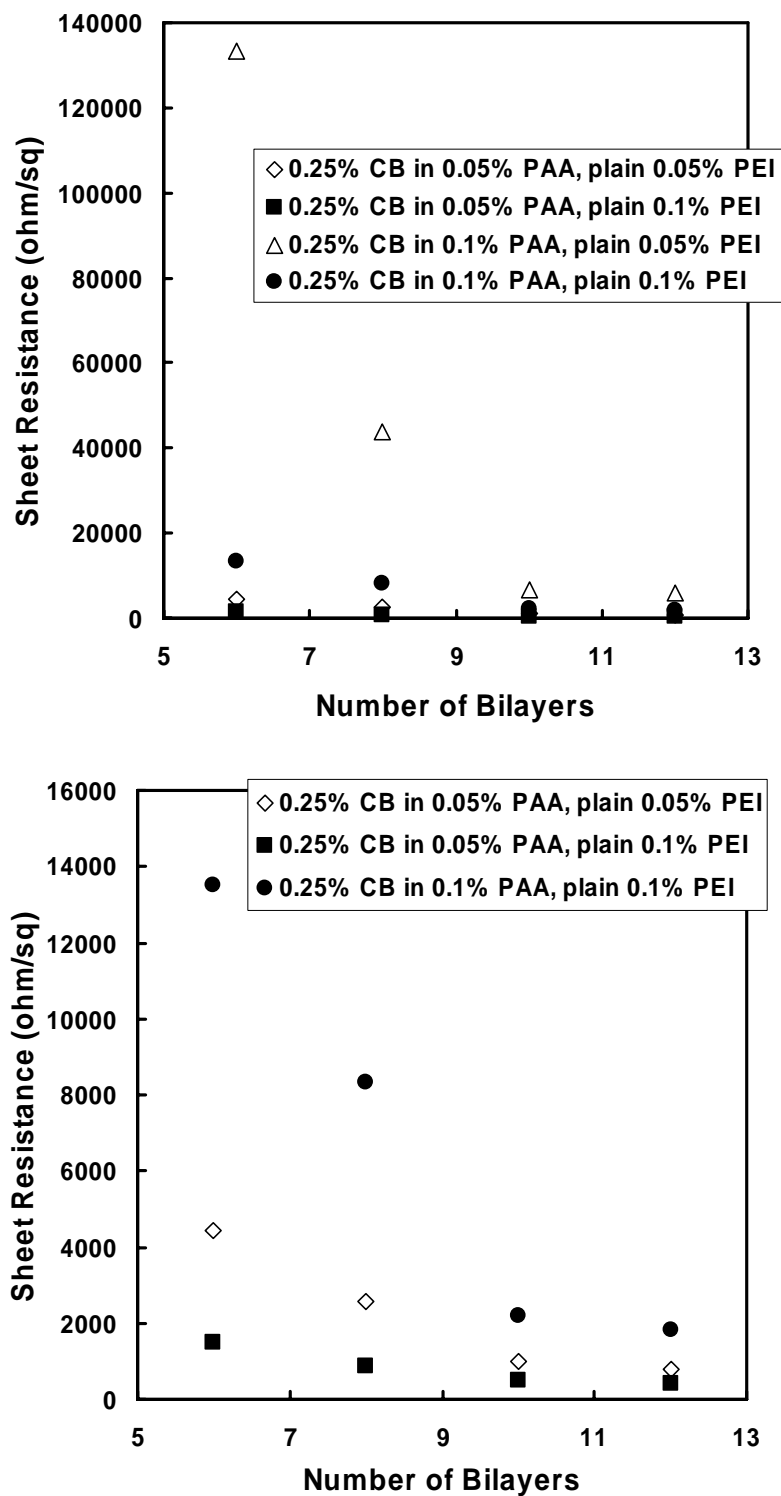


Figure 34. Comparison of sheet resistance values four series of films, carbon black is absent from PEI with different polymer ratios between mixtures. Standard deviation for all values less than 7%.

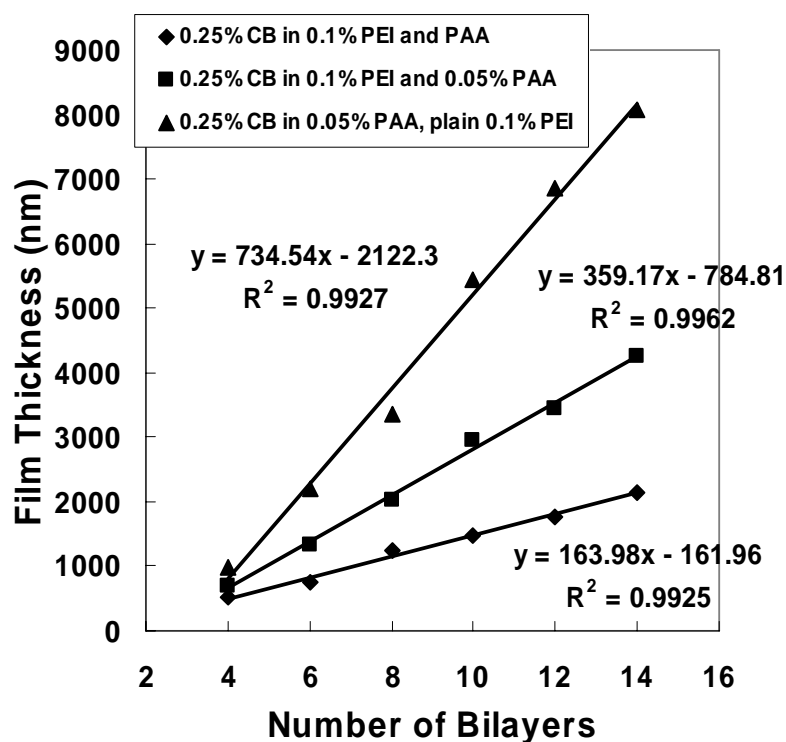


Figure 35. Thickness of films comparing three series: 0.25% CB in 0.1% PEI and PAA, 0.25% CB in 0.1% PEI and 0.05% PAA, and 0.25% CB in 0.05% PAA and plain 0.1% PEI. Standard deviation for thickness values less than 10%.

Bulk Resistivity

Improving electrical conductivity via optimized processing conditions and variation of composition was the goal of these experiments. In the processing variable experiments (Chapter II), the optimal bulk resistivity was found to approach $0.2 \Omega\cdot\text{cm}$. Despite achieving lower sheet resistance values (an order of magnitude below the values from the previous experiments), bulk resistivity did not improve. Table 1 and Table 2 compare all of the variables studied and show $0.2 \Omega\cdot\text{cm}$ to be the lowest achievable resistivity. Initially the films with lower values of sheet resistance exhibit lower values of bulk resistivity, but as the values for sheet resistance begin to level off at higher

bilayers, the values for bulk resistivity display the same trend. Even with the improvements in sheet resistance values, the general trend is that bulk resistivity will approach levels around $0.25 \Omega\cdot\text{cm}$ and a best of around $0.2 \Omega\cdot\text{cm}$. Figure 36 illustrates the difference in bulk resistivity values of all variable series.

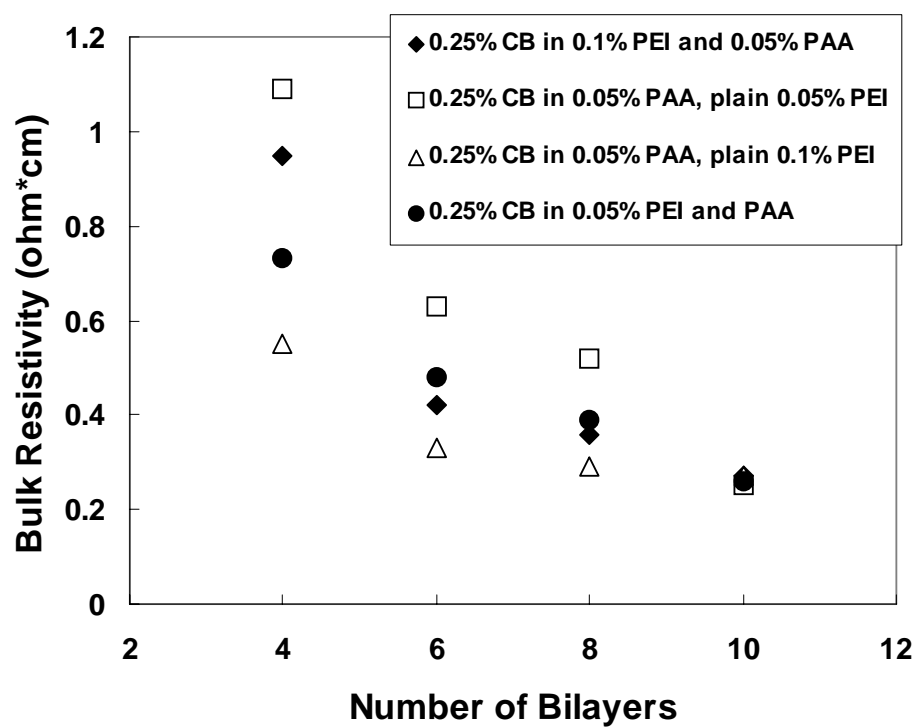


Figure 36. Optimal values of bulk resistivity.

Ionic Strength Manipulation

The final compositional variable studied was the ionic strength variation using NaCl. Varying the molar amounts of NaCl in the carbon black suspensions from 0.05 to 0.4 molar showed that any amount resulted in at least six times the level of sheet resistance. With the addition of NaCl to the mixtures, the ionic strength of the mixtures was increased [65-67], causing thicker films with a grainy texture. The addition of the

NaCl resulted in no positive benefits for the conductivity of these films, as shown in

Table 3.

Table 3

Ionic strength manipulation of original recipe and corresponding sheet resistance values found.

0.25% CB in 0.05% PEI and PAA Ionic Strength Manipulation		
Bilayers	Molar Amounts of NaCl	Sheet Resistance (Ω/sq)
8	0.05	338748.980
8	0.1	N/A
8	0.2	303144.750
8	0.4	81255.324
8	0.0	14469.194

Conclusions

Compositional variables were studied to further enhance conductivity once optimal processing variables had been found. Compositional changes included varying the concentration of polymer within the aqueous mixtures (with constant carbon black concentration), mixing and matching different polymer concentrations, intentionally leaving carbon black out of one of the mixtures, and altering the ionic strength of the mixtures by introducing different molar amounts of NaCl. Some new combinations of mixtures led to much lower values of sheet resistance compared with any values found during the processing variable experiments. It was found that films made with 0.25wt% carbon black in 0.05wt% poly(acrylic acid) (PAA) and plain 0.1wt% polyethylenimine (PEI) attained the lowest values for sheet resistance ($\sim 325 \Omega/\text{sq}$) which is an order of magnitude lower than the lowest sheet resistance value found from the original experiments ($\sim 1500 \Omega/\text{sq}$). Several other series also attained sheet resistance values $< 1000 \Omega/\text{sq}$ at 14 bilayers. When comparing values for bulk resistivity, it was found that

even with the lower values for sheet resistance, the increase in the thickness of the films counteracts them, resulting in a bulk resistivity floor at approximately $0.2 \Omega\cdot\text{cm}$. This consistency of bulk resistivity results in an overall consistent level of achievable conductivity with these processing variables as is. When different amounts of NaCl was added to the aqueous mixtures prior to film deposition, the resulting films had values of sheet resistance an order of magnitude higher than films not altered by NaCl. Altering the ionic strength of the mixtures creates charge screening effects that make the polymer chains more coiled and thickly deposited as a result.

CHAPTER IV

FUTURE WORK AND APPLICATIONS

Future Work

Producing electrically conductive thin films using layer-by-layer (LbL) assembly with carbon black was a success, but there are areas for improvement. Future work in this area includes eliminating the cracks prevalent in films with higher bilayers and optimizing the reproducibility of these films for possible commercial applications. Cracking is substantial when the thickness of films begins to approach 1500 nm. Figure 37 shows this for a 14-bilayer film that is approximately 8 μm thick.

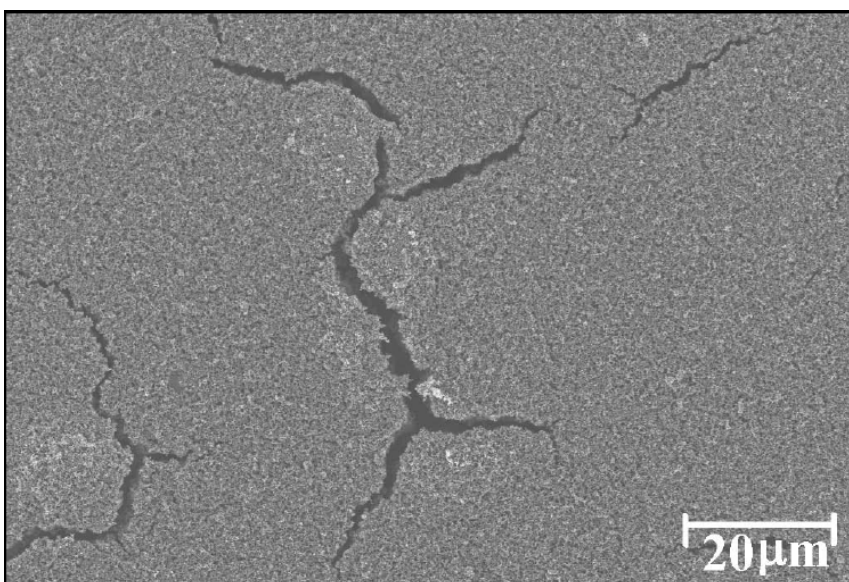


Figure 37. Significant cracking in a 14-bilayer film that is 8 μm thick.

One possible route to eliminate cracking is drying the films using critical point drying. Critical point drying is free of surface tension that generally exists from the evaporation of the water leaving the carbon black thin films. Eliminating cracks should

allow for further reduction in sheet resistance values in a linear fashion instead of tapering off. Making the deposition process more robust is key for future applications. The deposition process is generally done by hand and there is much room for improvement throughout the process. Inconsistencies permeate the process, beginning with the solution preparation and corona treatment and continuing to deposition time in each solution. Each small adjustment throughout the process can alter the results, giving a range of conductivities rather than one discrete value. This is a problem for commercial applications because reproducibility is desired to ensure similar results every time. Another item for future work is using Fourier Transform Infrared Spectroscopy (FTIR) with very little carbon black in the mixtures to determine if there is crosslinking occurring between the polyethylenimine (PEI) and the poly(acrylic acid) (PAA) upon heating. This is important because crosslinking will enhance the electrical conductivity due to densification of the structure [68,69].

Promoting adhesion on challenging substrates is another aspect of LbL film deposition that requires further study. Polyolefins, such as polyethylene (PE) are not very compatible with LbL deposition [70,71]. Our own initial studies with the carbon black system and clean PE showed patchy deposition coupled with poor adhesion to the particles [72]. With surface oxidized PE, the growth rate of the layers is improved, but at lower bilayers patchy deposition persists and somewhat poor adhesion is seen. PE particles that were oxidized and then grafted with multilayers of PEI exhibited stable growth of layers, excellent deposition coverage, and strong adhesion to the polymer particles. Figure 38 summarizes initial results found from these studies.

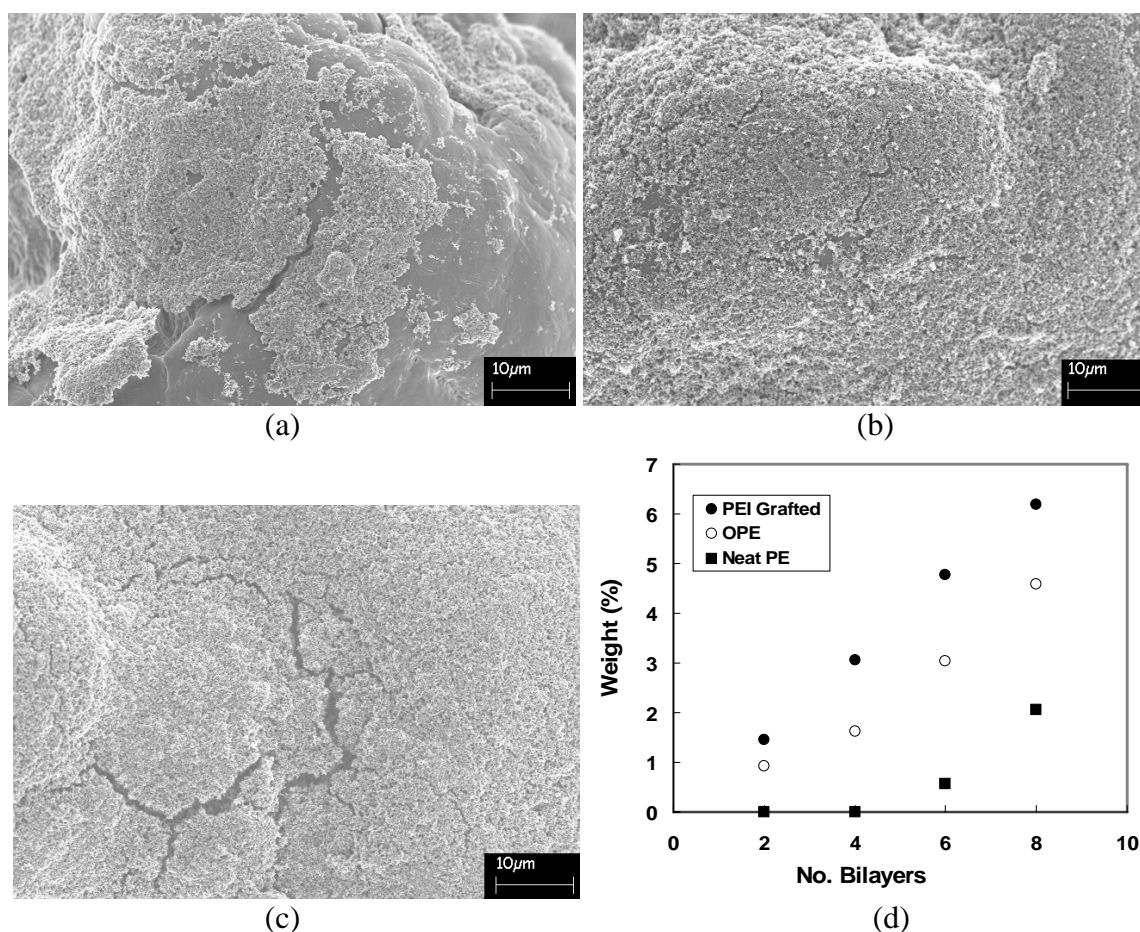
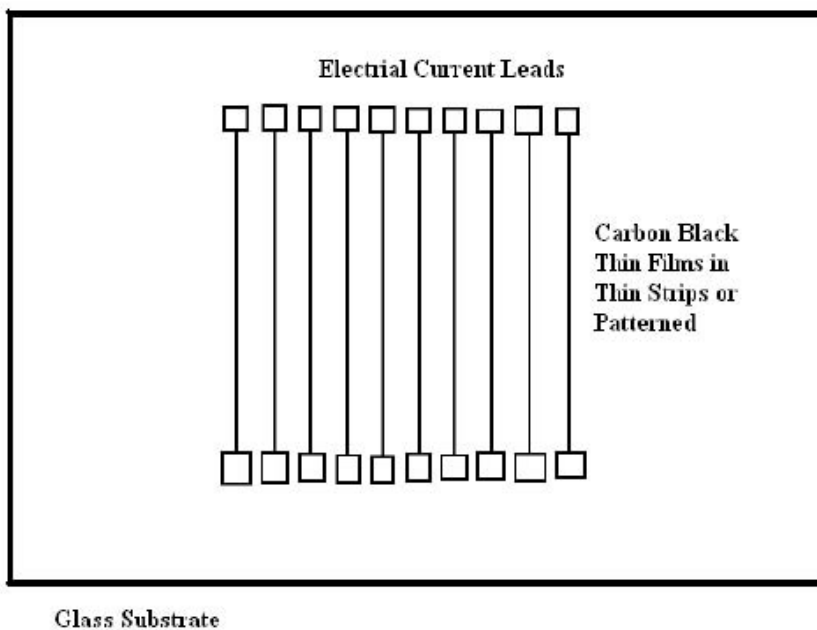


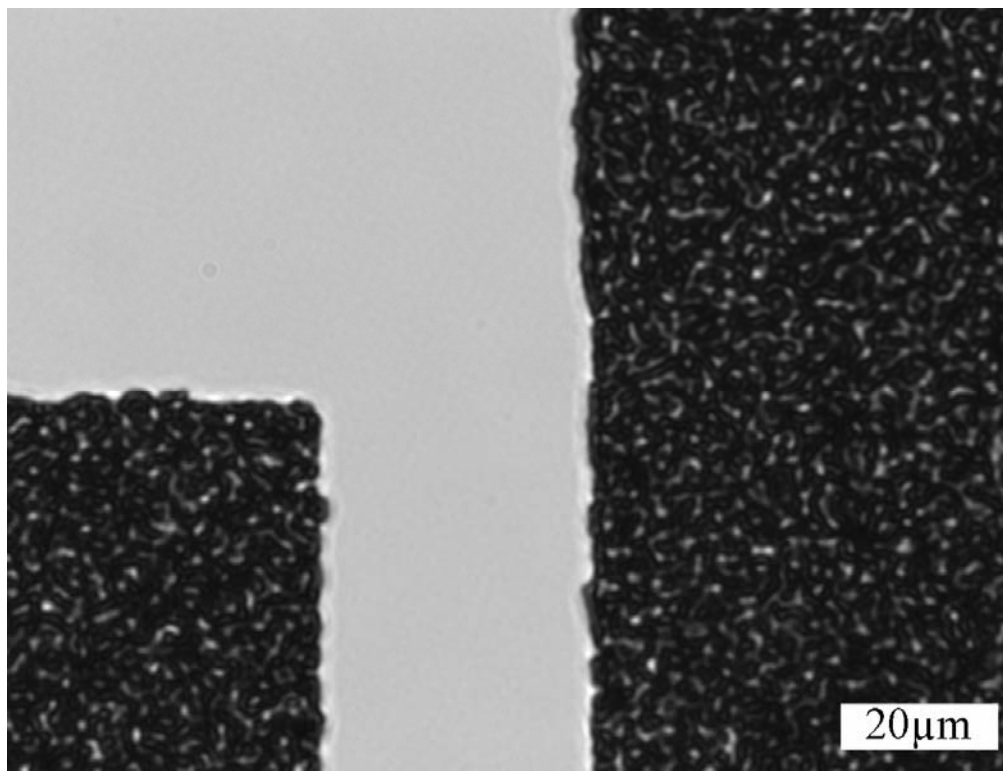
Figure 38. SEM images of deposition of 0.25% CB in 0.05% PEI and PAA on clean PE (a), surface oxidized PE (b), and PE particles oxidized then grafted with PEI (c). Concentration of carbon black on PE as a function of the number of bilayers deposited (a) [72].

Applications

With improvements, these electrically conductive films could be used for a variety of applications. One possibility is a resistive heater that can be made by patterning the thin films and applying a current across the pattern [73]. Since the films are conductive, adding a current will result in the generation of heat. Figure 39 shows a resistive heater design and an actual pattern made with LbL deposition of carbon black.



(a)



(b)

Figure 39. Schematic of resistive heater (a) and optical microscope image of patterned carbon black thin film (b).

Another possible application is sensing of things like humidity, temperature, and pressure. Bulk polymer composites filled with carbon black have been studied for decades in sensing applications [74-78]. Changes in humidity, temperature, or pressure will change the level of conductivity of the films. If the response to a certain stimulus is consistent, a relationship between changing resistance and the stimulus can be established to create a sensor. Other possible applications include using transparent carbon black thin films for low cost electrostatic dissipation in display applications or for light filtration.

CHAPTER V

SUMMARY AND CONCLUSIONS

Layer-by-layer (LbL) assembly was used to make highly conductive carbon black-filled polymer composite thin films. The effects of processing and composition effects were studied in an effort to decrease sheet resistance for a given number of bilayers. The processing experiments resulted in the lowest sheet resistance values when polymer-stabilized carbon black mixtures are sonicated prior to deposition and films are oven treated at 70°C for 15 minutes after deposition. As the number of bilayers was increased, film thickness grew linearly and the sheet resistance values decreased linearly up to 10 or 12 bilayers before leveling off. This leveling of sheet resistance was attributed to cracking in these thin films due to residual stress generated during drying. Oven treatment was found to lower sheet resistance values substantially and also to produce films 20% thinner than their non-oven treated counterparts. Films that are sonicated and oven treated can achieve a bulk resistivity of 0.2 $\Omega\cdot\text{cm}$ at 12 bilayers. Optically transparent films were produced by altering the pH of deposition mixtures, which resulted in thinner bilayers due to increased charge density on the stabilizing polyelectrolytes. This increased transparency is coupled with increased sheet resistance due to reduced film thickness and poor surface coverage.

Once the optimal processing variables for the lowest sheet resistance were determined, compositional variables were studied to further enhance conductivity. Compositional changes included varying the concentration of polymer within the

aqueous mixtures (with constant carbon black concentration), mixing and matching different polymer concentrations, intentionally leaving out carbon black from some mixtures, and altering the ionic strength of the mixtures by introducing different molar amounts of NaCl. It was found that films made with 0.25wt% carbon black in 0.05wt% poly(acrylic acid) (PAA) and plain 0.1wt% polyethylenimine (PEI) attained the lowest values for sheet resistance ($\sim 325 \Omega/\text{sq}$). Several other series also attained sheet resistance values $< 1000 \Omega/\text{sq}$ at 14 bilayers. When comparing values for bulk resistivity, it was found that even with the lower values for sheet resistance, the increase in the thickness of the films counteracts them, resulting in a bulk resistivity floor at approximately $0.2 \Omega\cdot\text{cm}$. When different amounts of NaCl was added to the aqueous mixtures prior to film deposition, the resulting films had values of sheet resistance an order of magnitude higher than films not altered by NaCl. Altering the ionic strength of the mixtures creates charge screening effects that make the polymer chains more coiled and thickly deposited as a result. These conductive thin films have several potential applications, including resistive heating, sensing, and electrostatic dissipation. Despite their potential, these carbon black thin films still require further optimization with regard to cracking, crosslinking, and adhesion to a variety of useful substrates. Even in the absence of future development, these films are the most conductive carbon black-filled polymer composites ever produced.

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VITA

Name: Chien Sy Jason Jan

Address: Air Liquide U.S., 2700 Post Oak Boulevard, Houston, TX 77056

Email Address: janman82@hotmail.com

Education: B.S., Aerospace Engineering, The University of Texas at Austin, 2004
M.S., Mechanical Engineering, Texas A&M University, 2006