ADHESIVE PROPERTIES OF WET POLYELECTROLYTE MULTILAYER FILMS
AND ELECTROPHORETIC DEPOSITION OF POLYELECTROLYTE COMPLEXES

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ABSTRACT

Weak polyelectrolyte multilayers prepared by using layer-by-layer (LbL) technique are known to become sticky upon contact with water and behave as a viscoelastic fluid, but the full extent of this wet adhesive property is not fully understood. In this study, the wet adhesive performance of polyelectrolyte multilayers consisting of branched poly(ethylene imine) and poly(acrylic acid) under controlled conditions was investigated by using a 90° peel test. The peel force is highest under neutral condition, and it decreases in acidic/basic environment. The addition of metal ions changes the peel force, either increasing it or decreasing it based on the nature of the metal ion. Addition of $\text{Cu}^{2+}$ stiffens multilayers, preventing multilayers from acting as an effective wet adhesive. The films are also characterized with zeta potential and shear rheometry, and the adhesiveness can be recovered by rewetting for at least 5 times. This polyelectrolyte based wet adhesive can be adhered to soft, wet surfaces like biological tissues such as liver. These multilayer films in this work show wet adhesive properties, however, the layer by layer technique used to fabricate these films requires several steps and take a long time. Therefore, new methods are needed to make these thin films. Spin-assisted LbL assembly, spray-assisted LbL assembly and electric field-assisted LbL assembly are widely studied because they are simple and time-saving. Electric field-assisted LbL assembly has been
gaining an increasing interest. One option for realizing this may be the electrophoretic deposition of weak polyelectrolyte complexes, made by mixing polyelectrolytes of opposite charge together, has not been studied yet. Therefore, electrodeposition of polyelectrolyte complexes under different conditions (i.e. pH, ratio of polycation and polyanion, concentration of polyelectrolyte complexes, concentration of salt and type of electric field) was investigated in this work. Polyelectrolyte complexes at moderate pH values and at the ratio of polycation and polyanion at 20 shows highest electrophoretic mobility. The thickness of polyelectrolyte complex film decreases with decreasing the concentration of polyelectrolyte complexes, concentration of salt and type of electric field) was investigated in this work. Polyelectrolyte complexes at moderate pH values and at the ratio of polycation and polyanion at 20 shows highest electrophoretic mobility. The thickness of polyelectrolyte complex film decreases with decreasing the concentration of polyelectrolyte complexes while the thickness increases when a proper amount of salt is added during preparing polyelectrolyte complexes. Under controlling pulse current at 10mA, a thicker film can be achieved but the surface is rougher compared with one prepared by using pulse potential at 10V. This work provides insight into both the wet adhesive properties of polyelectrolyte multilayers and electrophoretic deposition of polyelectrolyte complexes.
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CHAPTER I

INTRODUCTION

1.1 Layer-by-layer technique

The layer-by-layer (LbL) technique is a method of polyelectrolyte thin film fabrication with huge versatility and simplicity was found by Decher et al. Since then, this method has obtained much attention because it can be used to make films with a variety of materials including proteins, nanoparticles, or small molecules besides polyelectrolytes. Moreover, LbL is able to fabricate thin films or coatings on various surfaces with different shapes, such as glass, colloidal particles etc. Also, this method can be fast and practical with assistance of other techniques such as spin-coating approaches, spraying approaches as well as electrophoretic deposition techniques. To fabricate polyelectrolyte multilayer films via the LbL method, a substrate is immersed in polyelectrolyte solutions and sequentially adsorbs polyelectrolytes with complementary charges: polycation carrying positive charges and polyanion carrying negative charges. At each step, a reversal in charges of the surface occurs after adsorbing polyelectrolytes, which leads to a continuous assembly. The multilayer fabrication process can include various interactions, such as electrostatic attraction which is the main force for the strong
polyelectrolytes multilayer, hydrogen bonding as well as hydrophilic/ hydrophobic interaction which can play an important part on weak polyelectrolytes multilayer fabrication.\textsuperscript{13}

1.2 Polyelectrolyte

Polyelectrolytes, which are widely used during LbL assembly, are polymers with ionizable groups.\textsuperscript{14} These groups are able to dissociate under specific conditions, leaving charges on the polyelectrolyte chains and releasing small molecules i.e. counterions in solution. In most cases, the polyelectrolyte backbone is hydrophobic, and side groups with an ability of repelling each other are hydrophilic. Generally, there are two types of polyelectrolytes, one is strong polyelectrolyte which is fully ionized in the solution and regardless of pH of the solution, the other is weak polyelectrolyte, whose degree of ionization can be influenced by pH of the solution.\textsuperscript{15} For weak polyelectrolytes, they are partly charged in most cases and their ionization behavior can be described by using a parameter pKa, indicating pH at which half of side groups are dissociated and charged in the solution. The weak polyanion is more soluble at pH of solution above the pKa of polyelectrolyte and less soluble in solution when pH is lower than pKa, while the condition for weak polycation is opposite.

1.3 Polyelectrolyte complexes (PECs)

Polyelectrolyte complex, whose structure is shown in the scheme 1, is polyelectrolytes with opposite charges assembly held together by with electrostatic interaction as well as
secondary forces (i.e. hydrophobic force, Van der Waals’ force, hydrogen bonding etc.).

The composition, dimension, and structure of polyelectrolyte complex can be tailored by controlling several parameters such as pH, ionic strength and mixing ratio etc. Among several parameters, the mixing ratio is one of the important parameters controlling structure of PECs. When there is a great excess of one charge relative to the other, the complex is soluble and the mixture remains in the form of a one phase solution. When stoichiometries are more evenly matched, there is a liquid-liquid phase separation resulting in the formation of a complex coacervate.

![Scheme 1. Schematic illustration of polyelectrolyte–polyelectrolyte](image)

1.4 Zeta potential

A particle with net charges in solution has an influence on the distribution of ions surrounding it, shown in scheme 2, and the electrical double layer\(^{17}\) is defined as the region over the influence of the charged particle. Zeta potential is the potential at the surface of shear, which is an imaginary surface lying close to the solid surface and fluid within this surface is stationary.
Measurement of zeta potential is able to determine the magnitude of repulsive force between particles and the mobility of a particle. By measuring zeta potential, the ion distribution surrounding the particle can be analyzed and probability of particle coagulation can be expected.

Scheme 2\textsuperscript{17}. Schematic illustration of the distribution of ions surrounding a charged particle in the solution.

1.5 Adhesion fracture modes\textsuperscript{18-19}

Adhesion is an extremely complicated process, which focuses on the measurement of strength of similar or different materials that stick together. It is a state in which two materials are held together driven by interfacial forces, including valence forces formed via reaction of two materials, Van der Waals’ force and hydrogen bonding. With expanding needs of adhesive, adhesion behavior obtain an increase attention of researchers. A general term “Adherend” is widely used for various materials adhering to
a solid substrate, and a new term “adherate” defined by Mittal\textsuperscript{20} represents the material adhering to an adherend. As for adhesive, it is a special case of adherate because it adheres to two adherends rather than one, which means the adherate is sandwiched between two adherends.

1.5.1 Cohesive fracture

The adhesive is pressed between two substrates and the crack occurs within the adhesive during the peel test. There are adhesive on both substrates after the experiment.

1.5.2 Adhesive fracture

The crack appears at the interface of the substrate and the adhesive. When the adhesive is sandwiched between two substrates, the adhesive remains on one of substrates which adhesive has stronger affinity to after the experiment.

1.6 Different adhesion measurements

By detaching the film from the substrate normally or laterally to the substrate, experimentally adhesion can be measured in terms of external applied work or forces of separation of the adhering system. As mentioned before, separation may occur in adhesive, which is noted as cohesive fracture or at the interface of adhesive and substrate, known as adhesive fracture.
Several methods aimed at measuring the adhesion properties of materials is introduced as follows.

1.6.1 Direct pull-off (DPO) method

Belser and Hicklin\textsuperscript{21} measured the adhesion of metal films on glass. They first soldered a headed brass pin to the film and then applied a perpendicular force to pull the film with a pin in it. The force was measured by a spring balance.

However, such tests requires a perfect alignment and uniform stress distributions over the contact area is hard to achieve in the pulling process, which limits a wide application of this method.

1.6.2 Scotch tape method

Strong\textsuperscript{22} makes an attribution of this method. He used this method to measure the adhesion of aluminum films on glass. He pressed a pressure sensitive tape onto the film and stripped rapidly. However, there are some challenges of this method, one of them is that this test is highly qualitative and it is incomparable to other methods.

1.6.3 Peel test

The peel test has been widely used to measure adhesive strength. Spies\textsuperscript{23} was the first one to analyze the mechanics of elastic peel theoretically. During a peel test, a thin flexible strip is bonded to the substrate by adhesive and pulled off from the substrate at a certain angle.
The peel force is defined as the force required to separate the adhesive from the substrate.

The peel test is illustrated in scheme 3.

![Scheme 3. Schematic illustration of peel test.](image)

1.7 Ellipsometry

Ellipsometry is a technique which can detect the change of polarization (i.e. the phase difference $\Delta$ and the amplitude ratio $\Psi$) of the polarized light upon reflection of a sample. Generally, linearly polarized light becomes elliptically polarized after reflection from the sample surface. By measuring the change of the reflected light, ellipsometry can calculate the thickness of multilayer films. Besides the thickness, the roughness of films can also be determined by investigating the dielectric properties of the thin film.

A setup of an ellipsometry experiment is illustrated in scheme 4. An unpolarized light emitted from a light source passes through a polarizer so that a linearly polarized light beam is obtained. The polarization state of the beam can be decomposed to two electric fields, one is $E_s$ whose oscillating direction is perpendicular to the incident plane and the other is $E_p$, paralleling to the incident plane. Then beam reaches on the sample surface.
and the Es and Ep have different changes in Ψ and Δ after reflection. Ψ and Δ can be defined by using equation 1. Finally, the beam passes through an analyzer and obtained by a detector.

\[ \rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta} \]

Where \( r_s \) and \( r_p \) are coefficients representing amplitudes of Es and Ep components after reflection.

Normally, three incident angles (i.e. 65°, 70° and 75°) are chosen to run the measurement. The data are fitted by using a model consisting of a silicon layer, an intro layer, a SiO\(_2\) layer and a Cauchy layer representing the thin film. Mean Squared Error (MSE) as an estimator shows the difference between the calculation and experiment. A small MSE value means a good fitness.

![Scheme 4. Schematic illustration of an ellipsometry experiment](image)

1.8 Quartz Crystal Microbalance with Dissipation (QCM-d)

The Quartz Crystal Microbalance with Dissipation (QCM-d) is a technique which is widely used to determine the thickness of a film in a liquid environment. It is also able to investigate further properties of the film, most notably the softness of the film.
The QCM-d has a wide application in the areas of characterizing viscoelastic films\textsuperscript{24} build-up of polyelectrolyte multilayers,\textsuperscript{25-26} and corrosion of coatings.\textsuperscript{27}

A thin quartz crystal disk, which is sandwiched between two electrodes,\textsuperscript{28} is the active part of a QCM-d. AC voltage is applied over the electrodes to lead to an oscillation of the crystal. The oscillation decays exponentially as soon as the AC voltage is turned off. This decay is recorded and the energy dissipation factor (D) as well as the resonance frequency (f) are extracted.

Changes in the resonance frequency ($\Delta f$) implies the uptake or release of mass at the sensor surface, while changes in the dissipation factor ($\Delta D$) can indicate the viscoelasticity (softness) of the film and give information of changes in the structure of the film.\textsuperscript{29}

1.9 Electrophoretic mobility

A charged particle will move when it is placed in an electric field and a term “electrophoresis” is commonly used to describe the motion of charged particles in a liquid. $V_s$, an average velocity of particles, is proportional to the electric field strength $E$ at low field strengths, and the relationship between the velocity and electric field strength is expressed as $V_s = \mu_e E$, where $\mu_e$ is the electrophoretic mobility.

The electric field strength $E$ is given in units of volts/cm, and the velocity is given in units of microns/second. Therefore, electrophoretic mobility is given in ($\mu$/s)/(V/cm).
The sign of mobility indicates the sign of surface charges of particles. A positive mobility means the particle carries positive charges while a negative mobility shows a negatively charged particle. If a positively charged particle is mixed with a negatively charged particle, they can interact each other via electrostatic interaction and result in an unstable dispersion, which is possible to form precipitates.

The value of mobility can not only show how fast a charged particle to move under electric field, but also predict the stability of particles in a fluid. When the mobility is zero, the particle carry few charges on its surface and electrostatic repulsion is small, which results in aggregation of particles because of the existence of the attractive forces between particles. Higher mobility indicates more net charges on the surface of particles, resulting in a more stable solution because of electrostatic repulsion between identically charged particles.

1.10 Different types of electric field

During electrophoretic deposition, the type of electric field is one of important aspects which can be determined by the direction of electric field as function of time.

1.10.1 Direct current (DC)

The electric current has an unidirectional flow in direct current (DC). DC can be generated via batteries or rectifier which can convert AC to DC.
(a) Continuous potential and continuous current

Voltage or current is applied and the direction of flow remains the same over time.

(b) Pulse potential and pulse current

Pulse potential and pulse current can be produced by using a half-wave rectifier. The voltage or current of a pulse potential or pulse current wave continually changes over time but the sign of voltage or current is constant.

1.10.2 Alternating current (AC)

Alternating current (AC), produced by an alternator, demonstrates the flow direction of current varies periodically, compared with direct current (DC) with an unidirectional flow. There are several forms of AC, including sine wave, triangle wave, and square wave etc.
CHAPTER II
TUNABLE WET ADHESION IN POLYELECTROLYTE MULTILAYERS

2.1 Introduction

Synthesis of effective synthetic polymeric wet adhesives has been a challenging problem, due at least in part to the fact that the polymers will often interact more strongly with water than the desired substrate. While there are many potential biomedical applications for these materials, such as surgical adhesives, current commercial wet adhesives do have limitations. Surgical adhesives based on natural materials such as fibrin or collagen are difficult to produce and expensive, while synthetic adhesives based on cyanoacrylates or urethanes still suffer from low wet adhesion or the creation of inflammation in the body. Hydrogels often exhibit limited adhesive properties. These materials should be able to set under wet conditions and materials with different mechanical properties based on application are desirable. For example, a soft adhesive that is modulus matched to tissue or the desired substrate may have advantages in resisting failure of the joined interface in comparison to stronger adhesives. Self-healing adhesives could be useful by allowing for repositioning, and switchability of the degree of adhesion would allow for selective adhesion. A number of bio-inspired
strategies have been proposed, most notably taking inspiration from mussel adhesive or gecko feet, but these materials often require complex syntheses or fabrication. Presented here is a wet adhesive based on commercially available, synthetic polyelectrolytes, whose properties can be tuned based on pH and exposure to different ions, even to changing from adhesive to non-adhesive repeatedly. This system has already been demonstrated to have self-healing properties and can be reused by rewetting after dried.

Polyelectrolyte (PE) complexes and multilayers are materials formed by the complexation of oppositely charged PEs into films, coatings, dispersible particles, or even as bulk material. The layer-by-layer (LbL) technique, based on sequential exposure of a substrate to polycation and polyanion solutions, is a widely studied method to form polyelectrolyte multilayers (PEMs). The conceptually simple LbL process has various advantages over other thin film forming methods such as water based processing, controllable thickness, ability to incorporate multiple functionalities, and substrate determined morphology. Materials based on PE complexation combine the properties of both components, and have been suggested for use as sensors, actuators, biomedical devices, self-healable electrodes, energy storage devices, and surfaces with special wettability. These materials are generally considered to be suited to use in aqueous environments, where they are well hydrated although more dense than typical hydrogels, and as such are often considered for biomedical applications. One property of
some PE complexes and multilayers is their ability to function as a wet adhesive material. While this has been reported for some PEM system, much is still unknown about PEM wet adhesives and how to control their properties. One example of a wet adhesive PEM material is the weak PE branched poly(ethylene imine) and poly(acrylic acid) (BPEI/PAA) multilayer. Weak PEs are those containing labile functional groups that are environmentally sensitive, such as carboxylic acid or amine groups. Water is an extremely efficient plasticizer for PEMs, causing a rheological transition from a rigid, glassy film to a viscous, liquid-like material. Wet BPEI/PAA multilayers can serve as an adhesive that can be affixed to various types of substrates such as sheets of polystyrene, glass slides, paper, or aluminum foil regardless of surface charge or hydrophobicity. When using weak PEs the interpolyelectrolyte forces are readily modulated in response to surrounding conditions such as pH, presence of ions, and ionic strength. This can be used for controlling the adhesion of a BPEI/PAA film, which may be useful for the development of tunable, smart wet adhesives.

In this work, the wet adhesive performance of BPEI/PAA multilayers using different types of aqueous solutions. The interactions of different metal ions with PEs can dramatically influence physical properties of the PEM, and although there are studies on the assembly of PEMs with metal ions, there is still a great deal to be learned. A number of factors complicate the interactions of various metal ions and PEs, including coordination bond formation, ionic radius, hydration shell, and hydrophobicity of the ions.
Free-standing BPEI/PAA multilayer films were fabricated by the LbL technique, and their wet adhesive behavior was assessed by a 90° peel test using a BPEI/PAA film sandwiched between two pieces of aluminum foil. This test was performed under various conditions of pH and including different types of metal salts in the solution used to wet the BPEI/PAA film. The film can be modulated from low to high adhesive states by sequential exposure to different solutions. It was demonstrated that the wet multilayers are able to adhere to liver tissue, holding together pieces and closing cuts, showing potential application to wound healing. Furthermore, the wet adhesive property applies to both multilayers and complex coacervates of the PEs, which are even more easily prepared by simply mixing solutions of the two PEs and collecting the precipitate.

2.2 Experimental section

Branched polyethylenimine (BPEI, Mw = 25,000 g/mol), hydrochloric acid, sodium hydroxide, lanthanum(III) chloride heptahydrate, iron(III) chloride hexahydrate, silver nitrate, magnesium chloride, zinc chloride, sodium chloride, potassium nitrate, potassium chloride, 2,2-bipyridyl, and 1,10-phenanthroline were purchased from Sigma-Aldrich. Poly(acrylic acid) (PAA, M_w = 50,000 g/mol, 25 wt% aqueous solution), copper(II) nitrate hemi(pentahydrate), iron(II) chloride tetrahydrate and was purchased from Polysciences, Alfa Aesar, and Acros Organics, respectively. DI water with 18.2 MΩ cm resistivity from a Milli-Q filtration system (Millipore, Bedford, MA, USA) was used for
all experiments. All materials were used as received without further purification if there
is no specific notation.

Piranha solution was prepared by mixing 98% sulfuric acid with 30% hydrogen peroxide
at a volume ratio of 7/3. BPEI aqueous solution with the concentration of 80 mM
(respect to amine groups) and PAA aqueous solution with the concentration of 40 mM
(respect to carboxylic acid groups) were prepared by stirring overnight. Then, 1 M
hydrochloric acid was used to adjust the pH of BPEI solution to 9.5 and 1 M sodium
hydroxide was used to adjust the pH of PAA solution to 4.5. Both BPEI solution and PAA
solution were filtered prior to use.

2.2.1 Materials Fabrication

Latex spheres were prepared by using seeded semi-continuous polymerization with
methyl methacrylate (MMA), butyl acrylate (BA), and 2-hydroxyethyl methacrylate
(HEMA) as monomers applying Optimax (Mettler Toledo) working station as described
in previous work.\textsuperscript{79,80} Briefly, seed latex beads were first synthesized through batch
emulsion polymerization. After dissolution of 4.82 g sodium dodecyl sulfate (SDS), 0.81
g sodium bicarbonate, 112.60 g MMA and 48.10 g BA (molar ratio MMA:BA = 3:1) in
300.00 DI water at 60 °C under nitrogen protection, polymerization was initiated by
adding ammonium persulfate aqueous solution (0.81 g in 10.00 g DI water) and heated to
approximately 80 °C. As addition of ammonium persulfate is a heat releasing process,
temperature should be raised carefully to avoid overheating. HEMA-rich latex beads with
60 wt.% HEMA were then synthesized using the as-prepared seeds according to previous work.\textsuperscript{80,81} Seed dispersion was prepared by mixing 13.14 g seeds and 0.12 g sodium bicarbonate in 155.00 g DI water at 80 °C for 30 min. Monomer pre-emulsion for the shell was obtained by adding 20.18 g MMA, 25.82 g BA, and 69.00 g HEMA into 115 mL aqueous mixture of 0.46 g sodium bicarbonate, 0.80 g SDS and 0.58 g ammonium persulfate and stirred for 1 h. The monomer pre-emulsion was slowly fed into the reactor using peristaltic pump in 3.7 h. After completing feeding, the reactor temperature was raised to 90 °C for at least 1.5 h to ensure maximum conversion. All the process was proceeded under nitrogen protection.

The BPEI/PAA multilayer films were fabricated by LbL technique with a Zeiss HMS series programmable MICROM DS 50 slide stainer (Mercer Scientific Inc, USA) at room temperature.\textsuperscript{41} Clean polystyrene substrates were exposed to BPEI solution for 10 min and then were rinsed in three isolated DI water baths for 1 min each bath. Subsequently, they were immersed in PAA solution for 10 min and rinsed in three DI water baths for 1 min each. One BPEI/PAA bilayer was thus formed on polystyrene substrates. This BPEI/PAA deposition cycle was repeated for 50 times to form the desired multilayer films (denoted as (BPEI/PAA)\textsubscript{50}). After drying these films, they were peeled off the polystyrene substrates.

BPEI/PAA multilayers were coated on latex spheres by centrifugation assisted LbL process. Briefly, HEMA-rich latex spheres were first purified by dispersing in DI water,
centrifuging at 6,500 rpm for 15 min, and removing the supernatant prior to use. The collected latex spheres were redispersed in 30 mL BPEI solution by ultrasonicating for 5 min and vortexing for 15 min. The BPEI modified latex spheres were collected by centrifugation at 6,500 rpm for 15 min. The collected sample was then washed through repeating redispersion in 30 mL DI water and centrifugation at 6,500 rpm for 15 min for 3 times. Subsequently, the sample was modified with PAA layer through identical modification and washing process with PAA solution. After repeating \( n \) cycles of BPEI/PAA modification process, \( n \) BPEI/PAA bilayers were deposited on each latex sphere surface. BPEI/PAA coacervate was prepared by mixing BPEI solution (pH 9.5, 120 mM with respect to amine group) and PAA solution (pH 4.5, 120 mM with respect to carboxylic acid group) at volume ratio 1:1 by stirring overnight.

2.2.2 Characterization

The peel force of \( (\text{BPEI/PAA})_{50} \) films were measured using a 90° peel-off test by using the Texture Analyzer (Texture Technologies, MA, USA). Prior to measurement, the \( (\text{BPEI/PAA})_{50} \) film was sandwiched between two smooth aluminum foil substrates (6.75 cm\(^2\)), wetted with 200 µL selected solution, and equilibrated for 1 h. The excess solution was carefully removed using a piece of Kimwipe. The top substrate of the sample was fixed to the sample clamp, and the bottom substrate was fixed to a moving stage (shown in Figure S3). The peel force against displacement distance at a determined peel rate was recorded by the Texture Exponent 32 software. Stick-slip behavior was observed during
the peel test and a maximum force and minimum force could be seen at each stick-slip cycle. Here, the peel force of wet (BPEI/PAA)_{50} film was calculated in terms of the mean value of maximum forces of several cycles. The energy to separate the two substrates during the peel test was calculated by integrating the peel force-distance curve.

The effect of metal ion type, ion concentration and pH on adhesive force was studied by applying different solutions at a constant peel rate of 0.1 mm/s. For metal ion type study, 5mM metal ion solution of Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Ba\(^{2+}\), La\(^{3+}\), Zn\(^{2+}\), Ag\(^+\), Cu\(^{2+}\), Fe\(^{2+}\), and Fe\(^{3+}\) were used, respectively. For investigation of ion concentration effect, Na\(^+\), Cu\(^{2+}\), and Fe\(^{3+}\) solutions with concentration of 1 mM, 5 mM, 10 mM, 20 mM, 40 mM or 100mM were respectively applied. pH effect was tested with DI water adjusted to pH 3, 5, 7 or 9. Solution pH was adjusted with either HCl or NaOH but not both in order to avoid salt formation. For the reusability test, the BPEI/PAA sides of the peeled aluminum foils were wetted with DI water and pressed face-to-face for 1 h. After removal of excess water, the stuck sample was again subjected to 90° peel test.

The surface charge of (BPEI/PAA)_{4} coated latex spheres in various environment was measured by re-dispersing in related solutions and analyzed by Zeta-potential Analyzer (Brookhaven Instrument, USA). The particles were dispersed in DI water adjusted to different pH values (pH = 3, 5, 7, 9), and 5 mM metal ion solutions (Na\(^+\), K\(^+\), Mg\(^{2+}\), La\(^{3+}\), Zn\(^{2+}\), Ag\(^+\), Cu\(^{2+}\), Fe\(^{2+}\), Fe\(^{3+}\), pH 2.9), respectively.
Fourier transform infrared spectroscopy (FTIR) spectra were acquired by an Alpha-P FTIR spectrometer (Bruker Optics, Billerica, MA, USA) with attenuated total reflectance (ATR) mode. The samples were prepared by deposition of (BPEI/PAA)$_7$ on silicon wafer and analyzed after immersing in DI water with different pH (pH=3, 5, 7, 9) for 1 h and drying overnight.

The interaction of copper ions bound to various ligands and PEMs was studied by using solutions containing different molar ratios of copper ion and ligands. Specifically, 2,2-bipyridyl and 1,10-phenanthroline were used as ligands and stirred with copper ions overnight. Molar ratios of ligand to copper ions of 2:1, 1:1, 1:2, and 1:4 were used to test films at a peel rate of 0.1mm/s. In all of these ligand containing solutions the concentration of copper ions was 5mM and the pH of all solutions was adjusted to 2.9.

The swelling behavior of (BPEI/PAA)$_6$ film was monitored in situ by a variable angle spectroscopic ellipsometer (VASE, M-2000 UV-visible-NIR [240–1700 nm] J. A. Woollam Co., Inc., Lincoln, NE, USA) equipped with a temperature controlled liquid cell. The cell geometry dictated the angle of incidence to be 75°, and wavelength range was limited from 300 nm to 1050 nm for the recursive fits because of the absorption of solvents in the ultraviolet and near-infrared light region. Standard window correction protocols with a silicon wafer with thermal oxide (25.0 nm) as the reference were used prior to each measurement. The ellipsometry data were fitted by applying a four-layer model consisting of a silicon substrate layer, a fixed 1.0 nm Si-SiO$_2$ interface layer, a
0.8nm thermal oxide layer, and an effective medium approximation layer (with thickness, A and B free fit parameters) in Complete EASE (J. A. Woollam, Co., Inc., Lincoln, NE, USA). The PEM film was measured in situ from the dry state. After 1 min, related solution was carefully charged to the cell by using a syringe to avoid possible air bubbles, and ambient index for the related solution model was meanwhile applied to fit the ellipsometric data. All measurements were carried out at 25 °C.

Oscillatory shear measurements were proceeded on a strain-controlled Advanced Rheometric Expansion System G2 rheometer (TA Instruments, USA) equipped with an 8 mm parallel steel plate and a bath trap at a gap of ca. 0.030 mm at 25 °C. Angular frequency sweeps were acquired from 0.1 rad s\(^{-1}\) to 100.0 rad s\(^{-1}\) at strain amplitude of 0.50%, which locates in the stable strain% region.

To adhere the PEM to pieces of pork liver, the pork liver was first cut into equal size pieces. BPEI/PAA film was placed on one pork liver surface, and another pork liver piece was stuck onto the BPEI/PAA surface for 10 min. To close the cut notch in the tissue, BPEI/PAA film was wetted and then stuck onto one cut in the liver while the other notch cut into the piece of liver was left uncovered for comparison.

2.3 Results and discussion

Free-standing BPEI/PAA multilayers were prepared by the LbL method as illustrated in Scheme 5. By alternatively dipping a polystyrene substrate in cationic BPEI and anionic PAA solutions with intermediate de-ionized (DI) water rinsing steps, BPEI/PAA
multilayers were assembled, and the resulting films readily removed from the substrate due to the low strength of interaction between the hydrophilic PEs and the hydrophobic substrate. When wet with aqueous solutions, the swollen, plasticized film becomes a tacky, viscoelastic material, which is an adhesive that can be affixed to various substrates.

Scheme 5. Schematic illustration of the preparation process of free-standing BPEI/PAA multilayers and adhesive property upon wetting with water. The film is assembled onto a hydrophobic polystyrene substrate and then peeled off of it. For the peel test the film is sandwiched between two substrates (polystyrene shown here, but aluminum was used to gather the data presented in this work) and wet with an aqueous solution. One sees the characteristic fingering of the polyelectrolyte material associated with the adhesive remaining adhered to both surfaces while they are being pulled apart from one another.

While multilayers are used in the peel test studies presented here in order to precisely control the amount of material used in each test, it is important to note that complex coacervates of BPEI/PAA have the same wet adhesive properties. This material can be fabricated even more simply than multilayers, by mixing solutions of BPEI and PAA and then collecting the precipitate.
Figure 1 shows (a) a piece of polystyrene spread with BPEI/PAA complex coacervate that had been wet with DI water and (b) that a piece of aluminum foil can be attached to the polystyrene using the coacervate as a glue.

![Figure 1](image1.png)

Figure 1. Photographs of (a) BPEI/PAA coacervate spread on a polystyrene substrate, and (b) a piece of aluminum foil that had been stuck to that same polystyrene/coacervate surface being peeled back. One can see the fingering of the coacervate.

As a demonstration of wet adhesive ability, pieces of BPEI/PAA PEMs were used to glue together pieces of liver tissue, shown in Figure 2.

![Figure 2](image2.png)

Figure 2. (a) Pictures of freshly cut pork liver with two notches cut into the tissue. (b) a wet BPEI/PAA film was used to cover the left notch, allowing the hole to be closed while the right notch was left untreated. (c) Two pieces of pork liver are stuck to one another end to end using a wet BPEI/PAA film. The PEM is strong enough to hold the weight of the bottom piece of liver.
Tissue is wet and soft, making adhesion challenging. Pieces of pork liver were freshly cut, and the PEM can both adhere to them as well as hold together pieces of this tissue. Figure 2(a) shows a piece of pork liver with two notches cut into it. These notches upon up into holes pulled by the weight of the liver itself. Figure 2(b) shows the notch on the left being covered over by a wet BPEI/PAA PEM. The adhesive force provided by the PEM is sufficient to draw the sides of the notch together, closing the hole. The right notch remains untreated. Figure 2(c) shows two pieces of liver being glued together end to end; the PEM is strong enough to hold the weight of the bottom piece of liver tissue. Biological tissues such as liver have complex, charged surfaces, and charge-charge interactions between adhesive and liver tissue allow for formation of a bond.\textsuperscript{58}

Figure 3. Pieces of liver tissue sit out at room temperature for an hour. (a) One multilayer was attached to the left pork liver and pork liver on the right was not covered by multilayer as comparison. (b) Liver tissue after 1 h, showing no discoloration either with or without the PEM.

The PEM wet adhesive allows for a simple and effective way to assemble the pieces of tissue. The fact that weak PEs are components of this wet adhesive system means that the charge of the adhesive will change in response to proximity of the charged liver surface, making PE based adhesives potentially suitable for living, mutable systems. Also, the
application of the PEM does not discolor the piece of liver tissue at room temperature for over an hour. It has been shown that the application of some charged hydrogels to the surface of such a piece of tissue will discolor it, implying denaturing of the surface.$^{59}$ This does not happen with BPEI/PAA materials. Figure 3 shows side by side pieces of liver tissue sitting out at room temperature for an hour, one with the PEM adhered to it and one without. There is no notable difference between the two pieces, showing that the PEM does not create significant surface changes.

A 90° peel test, which measures the force required to pull apart two substrates affixed with the adhesive and is shown in Figure 4,$^{60–62}$ was used to probe the adhesive strength as a function of variation in pH and the ionic content of the solution used to wet the PEM.

Wet BPEI/PAA films generally demonstrate stick-slip behavior during the peel test, examples of which are shown in Figure 5, and failure typically occurs within the film with the film splitting internally (cohesive failure)$^{63}$ instead of detaching from the film/substrate interface. Scheme 5 shows the fingering of the wet adhesive which
typically occurred during the peel test. Because failure occurs cohesively in almost all cases (except for exposure to \( \text{Cu}^{2+} \) which will be discussed in more detail below) the peel force can also be taken as a measure of strength of the wet adhesive material itself.

![Figure 5. Peel force of (BPEI/PAA)\(_{50}\) wetted respectively by pH 2.9 water (a) and 5 mM \( \text{Fe}^{3+} \) solution (b) at peel rate 0.1 mm/s.](image)

To measure variation with pH, DI water adjusted to pH 3.0 to 9.0 was used. More extreme values of pH, either basic or acidic, were avoided for fear of dissolving the films.

![Figure 6. (a) Peel force and energy as a function of pH at peel rate 0.1 mm/s. There is a maximum in both at pH 7 (b) FTIR spectra of (BPEI/PAA)\(_{6}\) films treated by different pH water. It can be seen that carboxylic acid ionization changes only a small amount over this pH range.](image)
When wet with neutral water (pH 7.0), the film shows a maximum peel force of approximately 0.13 N (Figure 6(a)). The peel force decreases to ~0.10 N at pH 3.0 and ~0.087 N at pH 9.0. The calculated energies to separate the two adhered substrates are 0.71 mJ, 0.98 mJ, and 0.67 mJ at pH 3.0, 7.0, and 9.0 respectively. Therefore, the adhesive property of the film declines by either reducing or increasing pH of aqueous solution used to wet the film. This is similar to the pH dependent wet adhesion seen in polymethacrylic acid gels.64

These changes are due to the pH dependent ionization of both BPEI and PAA. The pKa of PAA is ca. 6.5,65 while BPEI possesses three pKa values (4.5, 6.7, and 11.6) due to the presence of primary, secondary, and tertiary amine groups.66 In the as-prepared dry film, BPEI and PAA are both partially charged with a moderate ionic crosslink density that allows the film to swell and for a good degree of chain mobility. At lower pH, the BPEI amine groups are more charged and the PAA carboxylic acid groups become protonated and therefore neutral. At higher pH, the reverse is true: the BPEI is less charged and the PAA is more charged. As a result, the total number of ionic cross-link points are reduced and adhesive force is weakened. To measure the surface charge of BPEI/PAA under different pH conditions, BPEI/PAA multilayers were assembled on negatively charged HEMA-rich latex spheres. The zeta potential of the BPEI/PAA coated latex spheres is –25 mV in neutral water, and it becomes more negative after incubated in pH 9.0 water (Figure 7(b)). In lower pH water, the zeta potential in turn appear as positive, and the
lower the pH is, the more positive the zeta potential. This indicates that the PAA and BPEI chains in BPEI/PAA multilayers are more charged in basic and acidic environments, respectively.

![Graphs showing zeta-potential of BPEI/PAA multilayers coated latex spheres as functions of bilayer number, pH of water, and metal ion types in ion solutions.](image)

Figure 7. (a) Zeta-potential of BPEI/PAA multilayers coated latex spheres as functions of bilayer number, (b) pH of water, (c) and metal ion types in ion solutions. The concentration of metal ion solution was fixed at 5 mM.

The ionization degree of carboxyl group in the as-prepared BPEI/PAA film under different pH environment was calculated based on asymmetric stretching band of COO$^-$ at $\nu = 1565–1542$ cm$^{-1}$ and C=O stretching of COOH at $\nu \sim 1710$ cm$^{-1}$ in the related FTIR spectra (Figure 6(b)). As this two bands from same sample is assumed to have the same extinction coefficients, the degree of ionization of PAA at a determined pH was calculated as following equation:

$$\text{Degree of Ionization} = \frac{A_{\text{COO}^-}}{A_{\text{COOH}} + A_{\text{COO}^-}} \times 100\%$$

(1)

where $A$ indicates absorption band intensity. By increasing pH value, the degree of ionization of PAA increases from 56.5% at pH 3.0 to 68.3% at pH 7.0, but it remains
essentially unchanged at higher pH condition, which is consistent with the results reported by Rubner and his co-workers.\textsuperscript{65} Although one might expect a larger change in carboxylic acid ionization over the range of pH 3.0–9.0, the PAA charge density is strongly influenced by its surrounding environment such as the PEM. It has been shown that over this pH range the carboxylic acid ionization for a linear poly(ethylene imine)/PAA multilayer is relatively constant,\textsuperscript{65} showing that the PEM environment acts as a buffer over this range. Accompanying the change of PAA charge density, BPEI becomes more charged at low pH and less charged at high pH,\textsuperscript{68} but it is difficult to quantify the degree of ionization of amine groups in BPEI from the FTIR spectra because the adsorption bands of the various amine groups overlap with those of PAA and bands associated with the polymer backbones.\textsuperscript{69}

Figure 8. Peel force and energy as a function of 5 mM different metal ions at peel rate 0.1 mm/s. The blue line represents the peel force when using DI water and is meant as a guide to the eye to easily identify which ions reduce the force and which ions increase the force.
Various metal salts were added to the solution used to wet the multilayer, and the effect of these different metal ions on the peel force and energy is summarized in Figure 8. To avoid hydroxide formation the pH for all 5 mM metal salt solutions was fixed at 2.9, which is the same as that of the as prepared FeCl₂ solution.

Compared with DI water also adjusted to pH 2.9, the peel force and energy for the wet adhesive BPEI/PAA films decreases by adding Na⁺, K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Zn²⁺ or Cu²⁺, while these values increase upon exposure to Ag⁺, La³⁺, Fe³⁺ and Fe²⁺ ions. This observation agrees with reports of increased adhesive forces for biopolymer containing PEMs in the presence of Fe³⁺. Although different anions are reported to impact on PEM properties differently, the same peel force and energy were measured within experimental error for the samples applied with potassium, sodium, and copper chloride and nitrate salts (Figure 9).

Figure 9. Peel force and energy of a BPEI/PAA film wet with aqueous solution containing 5 mM salt. (a) KCl and KNO₃, (b) NaCl and NaNO₃, (c) CuCl₂ and Cu(NO₃)₂.
For alkali and alkaline earth metals (Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, and Ba$^{2+}$), the trend in peel force matches with the zeta potential of BPEI/PAA PEMS exposed to the ion solutions (Figure 7c), while it is not well-correlated with hydration radius. These alkaline metal ions primarily interact with PAA through electrostatics in the film, which partially weaken or dissolve ionic cross-links through charge screening, increasing chain mobility. While monovalent ions interact with only a single anionic carboxylic acid group, divalent ions are able to form bridges across two carboxylic acid groups which in turn restricts the chain mobility. It can be said that divalent alkaline metal ions reduce the peel force to a greater degree than the monovalent ions do.

The situation for transition metal ions is more complex. As well as interacting through electrostatics, these ions can form coordination bonds with the PEs having a covalent nature. Zn$^{2+}$ behaves similarly to the alkali ions (reducing adhesion), while the other transition metals with the exception of copper increase the strength of the wet adhesion. In the cases where the peel force is increased, it can be inferred that the formation of coordination bonds increases the internal forces within the PEM, increasing the amount of force required to pull the PEM apart. For most cases described (both changing pH or metal ions), the wet BPEI/PAA PEMS fail within the film during the peel test (cohesive fracture), but when exposed to copper ions failure occurs at the interface of the aluminum foil substrate and the film (adhesive fracture). Copper exposed films have the lowest peel force, at roughly half the peel force of water treated films, and become
much stiffer. Also, there is no fingering of the PEM wet with copper containing solution when the substrates are pulled apart. The change in mechanical properties upon exposure to copper ions is different even than for the other metal ions that reduce the peel force. It is only in the copper case that the film becomes stiff. This indicates that the internal forces in the Cu\(^{2+}\) treated film become stronger than the adhesive force between the film and the foil substrate, in contrast to the PEMs treated with other metal ions or pH values. It is known that Cu\(^{2+}\) ions have an extremely high affinity with both amine and carboxylic acid groups,\(^\text{71}\) and can coordinate with the amine and carboxylic acid groups. The cross-links restrict the relaxation and mobility of PE chains, stiffening the film, making it not a good adhesive. At this concentration, only exposure to Cu\(^{2+}\) creates this phenomena.

In response to immersion in water, the BPEI/PAA film quickly swells. The uptaken water serves as plasticizer and facilitate relaxation of PE chains, which turns the initially glassy solid into a viscoelastic gel.\(^\text{41}\) The rheological behavior of free-standing BPEI/PAA films in pH controlled water or metal ion aqueous solution (pH 2.9, 5 mM) is presented in Figure 10.

Upon exposure to different pH water, the BPEI/PAA film exhibits loss modulus (G’’) generally higher than storage modulus (G’’) over the tested angular frequency region (0.1~100.0 rad/s), although at pH 5 this difference is small (Figure 10(a)). Both moduli are proportional to angular frequency without reaching a plateau value, demonstrating
liquid-like flowable nature of the wet BPEI.PAA film. The film has the highest moduli (both $G''$ and $G'''$) when exposed to pH 7.0, lesser at pH 5.0, and the least at pH 3.0 and 9.0, which corresponds to the trend in adhesive property. It can be concluded that the films with lower moduli have weaker internal forces and fail more readily during the peel test.

Figure 10. Angular frequency sweep of storage modulus and loss modulus of (BPEI/PAA)$_{50}$ films soaked in different pH water (a), aqueous solutions containing transition metal ions (b) and alkali metal ions (c). Closed symbols are the storage modulus and open symbols are the loss modulus. (d) Angular frequency sweep of free-standing (BPEI/PAA)$_{50}$ film in pH 2.9, 5 mM ions. (e) Complex viscosity of films wet with various metal ions at angular frequency 0.5 rad/s at 25 ºC as a function of metal ion.

Upon addition of alkali metal ions, a slight decrease is observed in both storage and loss moduli compared with that in pH 2.9 water, but the loss modulus still dominates over the monitored angular frequency region. While this result indicates the wet film flows, the
film becomes mechanically weak, and it collapses and deswells in these alkali metal ion solutions. This can be seen by ellipsometry, shown in Figure 11. This phenomenon originates from the charge screening effect by alkali metal ions, which compensate negatively charged carboxylic acid groups and partially break the initial ionic bonds between PE chains. This is consistent with previously observed salt softening effect on PEMs,\textsuperscript{72} and the adhesive property is also weakened as a result.

Figure 11. Swelling behavior of (BPEI/PAA)\textsubscript{6} film in (a) water, KCl solution, MgCl\textsubscript{2} solution, LaCl\textsubscript{3} solution, (b) and AgNO\textsubscript{3} solution, Cu(NO\textsubscript{3})\textsubscript{2} solution, Fe(NO\textsubscript{3})\textsubscript{3} solution. The initial dry thickness is \(\sim\)300 nm. Solution pH was adjusted to 2.9.

For transition metal ions, again multiple effects are observed. Storage and loss moduli of the PEM drop when in Ag\textsuperscript{+} solution, remain similar or are even slightly higher compared to those in water when exposed to Fe\textsuperscript{3+} and Fe\textsuperscript{2+} solutions, and increase significantly in Cu\textsuperscript{2+} solution. With the presence of Cu\textsuperscript{2+}, the storage modulus dominates from 0.1 rad/s to 100.0 rad/s, showing a stiff, solid-like nature. This is a result of the additional bonding and the strength of that bonding between both PEs and the copper ions. This transition to a rigid material (\(\tan \delta\) 0.19 at angular frequency 0.5 rad/s) that occurs in the presence of
Cu\textsuperscript{2+} explains the low adhesion of the PEM in that environment. Relaxation of the PE chains in this case is highly restricted and failure in the presence of Cu\textsuperscript{2+} occurs at the foil/PEM interface instead of within the PEM as with the other cases. While silver treated films show lower moduli, the Ag\textsuperscript{+} treated films are lossier (tan δ 2.08 at 0.5 rad/s) than films wetted by water (tan δ 1.64 at 0.5 rad/s).

Figures 10(d) and (e) represent the magnitude of the complex viscosity of the PEM soaked in different metal ion solutions over the entire frequency range and at 0.5 rad/s, respectively. Although it is also not a perfect predictor of peel force, one can make several observations. Complex viscosity contains both viscous and elastic components. The very large value of complex viscosity for the Cu\textsuperscript{2+} treated films reflects the elastic, solid-like nature of that film. The significantly high complex viscosity shows that the Cu\textsuperscript{2+} treated film is no longer compliant, resulting in early failure at the interface between the PEM and the substrates. With a couple of exceptions, for exposure to the ions other than copper the more viscous the higher the peel force. For example, Fe\textsuperscript{2+} and Fe\textsuperscript{3+} have the highest peel force values and the highest complex viscosity values. Zinc ions result in the lowest peel force and the lowest complex viscosity. All of these materials have a much lower complex viscosity value than the copper ion treated films. Barium and calcium ions, however, do not follow the trend but overall complex viscosity has a better correlation to peel force for the metal ion treated films than either loss or storage modulus do. This shows that adhesiveness depends not only the density of ionic
cross-links but also PE chain mobility, and rheological data gives some insight into the adhesive behavior of viscoelastic film.

Figure 12. Peel force and energy as function of salt concentration of pH 2.9 aqueous solution containing (a) Na\(^+\), (b) Cu\(^{2+}\) and (c) Fe\(^{3+}\) at peel rate 0.1 mm/s.

Figure 12 presents the correlation between peel force as well as energy with the concentration of alkali ion (Na\(^+\), figure 12(a)) and transition metal ions (Cu\(^{2+}\) figure 12(b), Fe\(^{3+}\) figure 12(c)). By increasing the concentration of Cu\(^{2+}\), the peel force as well as energy of the film further decreases, being decreased from 0.073 N and 0.56 mJ in 1 mM Cu\(^{2+}\) to 0.046 N and 0.32 mJ in 100 mM Cu\(^{2+}\). With an increased density of Cu\(^{2+}\) containing coordination bonds, the BPEI/PAA film becomes even stiffer resulting in even earlier failure during peel test. A similar decrease in peel force of BPEI/PAA film is observed by increasing Na\(^+\) concentration in the applied aqueous solution, but the Na\(^+\)
treated films are always more adhesive than Cu$^{2+}$ treated ones. Starting from \textit{ca.} 0.12 N in 1 mM Na$^+$ solution, the peel force gradually decreases to 0.063 N in 100 mM Na$^+$ solution. For Fe$^{3+}$ treated films, the peel force and energy increase from 0.07 N and 0.54 mJ in 1 mM Fe$^{3+}$ to 0.136 N and 1.02 mJ in 10 mM Fe$^{3+}$, which is consistent with the idea that coordination bonds can enhance internal forces within the PEM. By further increasing the concentration of Fe$^{3+}$, however, the peel force and energy decline to 0.054 N and 0.40 mJ in 100 mM Fe$^{3+}$. At these higher concentrations the Fe$^{3+}$ treated films become stiff in a manner similar to the Cu$^{2+}$ treated films. The failure mode also changes in this case, with the film failing at the substrate/PEM interface (as in the Cu$^{2+}$ treated case) and no longer within the PEM. This shows that these multivalent transition metal ions behave in a similar manner, but with a lower concentration of Cu$^{2+}$ being able to create this stiffness in the PEM. It can be inferred that Cu$^{2+}$ is able to bind to the amine and carboxylic acid groups in a qualitatively different way, perhaps forming less labile, stiffer, or stronger coordination bonds.

As the metal ion interactions are reversible,\textsuperscript{73} it is possible to control the cross-link density and adhesive behavior by adding chelators. Small molecule ligands, 2,2-bipyridyl and 1,10-phenanthroline, were added to the aqueous solutions of Cu$^{2+}$ ions. These molecules are expected to bind with two of the six available copper sites. When either chelator is added, both peel force and energy increase monotonically with the addition of chelator molecules (Figure 13(a) and (b)). When an excess of chelator molecules were
added (chelator : Cu$^{2+}$ ratio = 2:1), the peel force becomes almost comparable to that measured by using DI water alone to wet the film. This same result is observed at both pH 7.0 and 2.9. These data show that small molecule chelators can be used to further tune the wet adhesive properties of PEMs. Additionally, the wet adhesive property of a single BPEI/PAA film can be turned on and off by alternately using copper and chelator solutions. Exposing a film to copper ions makes the film stiff and a poor adhesive, which can be reversed by exposure to a solution containing only one of the chelators mentioned above. One can cycle between on or high adhesion and off or high adhesion states, as represented in Figures 13(c) – 13(h) showing the PEM sandwiched between two pieces of aluminum foil and those pieces of foil then being pulled apart. When the film is an effective adhesive, one can see the “fingering” between the two substrates, when stiffened with Cu$^{2+}$ there is no fingering. Figure 13(c) shows the sticky film wet with DI water, figure 13(d) shows the film wet with copper ion solution and no fingering, and figure 13(e) show that film have been soaked in a 2,2-bipyridyl solution and again behaving as a wet adhesive. Furthermore, adhesion can also be toggled between sticky, high adhesion and stiff low adhesion by sequential exposure to iron and copper ions. Figure 13(f) shows the sticky property of the film when wetted with an iron ion solution, then 13(g) shows the film no longer being an adhesive after exposure to copper ions, and 13(h) shows the film becoming sticky by once again being exposed to iron ion solution. This shows that copper ions can displace iron ions that have been bound within the film, but also that iron can again displace the copper bonds. This change of environment
toggles between low and high adhesion states as well as mechanical properties, going from stiff to sticky and back. There are reports of using pH, light, and temperature to control wet adhesion, but response to metal ion more unusual, with previous reports using polymers with chelating moieties incorporated into them.

Figure 13. The peel force and energy of BPEI/PAA multilayers as function of molar ratio of (a) 2,2-bipyridyl/Cu\(^{2+}\) (b) and 1,10-phenanthroline/Cu\(^{2+}\) at a constant peel rate of 0.1 mm/s. The pH of chelator/Cu\(^{2+}\) solution was fixed at 2.9, the concentration of Cu\(^{2+}\) was fixed at 5 mM. Image (c) shows a film was wetted by DI water, then sequentially exposed to (d) copper ions (e) and chelator solution. One can see the characteristic fingering of the adhesive material in part (e) but not in part (d) when the film was exposed to copper ions. Part (f) again shows a sticky film that was wet with copper ion solution, then the ability to toggle the adhesive property from high to low adhesion with exposure to (g) copper ions and (h) iron ions once again.
The peel force and energy measured using wet BPEI/PAA films in pH 7.0 water at different peel rates are summarized in Figure 14.

At low peel rate (0.02 mm/s), the peel force and energy appear to be 0.05 N and 0.29 mJ, respectively. Both of these parameters increase steadily upon increasing the peel rate, reaching 0.44 N and 2.44 mJ at 1.00 mm/s, which is roughly about 10 times of those at 0.02 mm/s. This result agree with previous observations, in which peel force increases with accelerated peel rate.75,76

![Figure 14. Peel force as function of peel (left column) and energy (right column). (a) BPEI/PAA film in DI water and (b) pH 2.9.](image)

The overall peel force can be thought to involve two factors: bending force and adhesive force.63 When the peel rate increases, the radius of curvature of the aluminum foil substrate decreases, and the resulting larger bending moment of the substrate contributes in increasing the overall force.
Once the aluminum foil substrates attached by BPEI/PAA multilayers are separated from each other, the PEM covered sides are no longer adhesive. However, by simply re-wetting with DI water they can be made to be sticky once again.

Figure 15. Peel force and energy of (BPEI/PAA)$_{50}$ film through repeated peel test at 0.1 mm/s and DI water treatment. By rewetting the film, it is possible for it to be reused as a wet adhesive. Reduction in peel force of less than 10% is attributed to minor loss of material through the repetition of the experiment.

As shown in Figure 15, the first peel force required to separate the attached pieces aluminum foil is 0.106 N, and it remains similar in value at 0.096 N to separate them a second time after rewetting the adhesive. After 4 times of peel/recovering treatment, the peel force is kept as 0.084 N. A slight decrease in both peel force and energy is observed, which is most likely due to the loss of some of the wet adhesive material through the repeated wetting, pulling, and re-wetting.
This recoverable wet adhesive nature originates from the water triggered migration of weak PE chains.\textsuperscript{41} The water triggered sticky behavior of BPEI/PAA can be imagined for use as an environmentally benign adhesive that is reusable. BPEI/PAA multilayers are classified as “exponentially“ growing multilayers, meaning that there is a good deal of chain mobility and diffusion throughout the PEM, leading to a homogeneous structure throughout, somewhat different than that created by strong PEs.\textsuperscript{77} This uniformity is similar within the BPEI/PAA complex coacervate material, explaining why they basically have the same wet adhesive properties.

2.4 Conclusion

BPEI/PAA PEMs and complex coacervates are shown to be effective wet adhesives, for example being able to stick together pieces of biological tissue. These materials have previously been shown to have self healing properties. It was demonstrated that although the films lose stickiness when dried, they can be re-wetted and reused as an adhesive a number of times. The adhesive nature can repeatedly be turned on and off from low to high by sequentially exposing the BPEI/PAA material to solutions of copper ions and small molecule chelators or even copper ion and then iron ion solutions. This switching also changes mechanical state, from a stiff film to a soft, sticky material.

The wet adhesive performance of BPEI/PAA PEMs wetted with aqueous solutions of different pH as well as containing different metal ions is studied here using a 90° peel test. The films demonstrated stick-slip behavior and failure occurred within the adhesive
and not at the interfaces in almost every case. The peel force is highest when the film is wet with neutral pH water, and it declines under either acidic or basic conditions. One can conclude that there is an optimal amount of crosslink density and PE chain mobility that preserves chain mobility but also gives high enough internal forces that then results in maximum wet adhesive force. Interactions with various metal ions have a strong influence on the adhesiveness of the BPEI/PAA material, in some cases creating a more adhesive material and in some cases reducing the adhesive nature. Transition metal ions interact very differently with PEMs than alkali metals or alkaline earths. Exposure to Cu\(^{2+}\) ions greatly stiffen the BPEI/PAA materials at concentrations much lower than any other metal ion. Rheological measurements show that films that are stiff or have very high complex viscosities are not good adhesives, and some amount of compliance/viscoelasticity is required. However, rheology is not a perfect predictor for metal ion exposed films, showing that electrostatics and other interactions complicate the physical properties of these films. Zeta potential is a good (but also not perfect) predictor of peel force for the metal ion cases.

The currently developed BPEI/PAA adhesive is superior to previously reported adhesive containing strong PEs\(^\text{78}\) as the wet sticky BPEI/PAA is capable of adhering various substrate regardless of the surface wettability and surface charge\(^\text{41}\) while the application of the strong PEs based adhesives is limited to negatively charged hydrophilic surfaces\(^\text{78}\). One can envision further functionalization of these films by loading drugs into them,
which is already well established using polyelectrolyte multilayers.⁷⁹ BPEI/PAA materials have great potential for practical applications in such areas as wound healing, controlled drug delivery, and other biomedical uses.
CHAPTER III

A NEW METHOD TO PREPARE THIN FILMS VIA ELECTROPHORETIC DEPOSITION OF POLYELECTROLYTE COMPLEX

3.1 Introduction

Polyelectrolyte complexes (PECs), a versatile category of materials, are made when oppositely charged polyelectrolytes are mixed together via ionic crosslinks, driven by entropic increase of releasing counterions. Michaels et al. firstly investigate the properties of synthetic polyelectrolytes. Ever since then, interests in PECs have been boosted. PECs have been widely used as coatings and binders. Also, PECs have been applied as microencapsulation and proton exchange membranes.

Many studies have investigated the fundamentals of PECs formation. PECs can form quasisoluble or solution-precipitated complexes during mixing polyelectrolyte solutions carrying opposite charges under different conditions. The final morphology of PECs can be tailored by controlling concentration, chemical composition as well as ionic strength. Also, the stoichiometry of various constituents can play an important role in controlling the morphology of PECs. PECs are in physically rugged precipitates if positive and negative repeating units are matched, however, PECs are soluble and
remains in one-phase solution when there is one charged polyelectrolyte greatly excessive than the other. The same polyelectrolytes can be deposited on a substrate by alternately immersing the substrate into solutions to obtain polyelectrolyte multilayer films (PEMs). By comparing with PEMs, PECs have advantages in easy preparation and time-saving. Moreover, PECs prepared by using desired polyelectrolytes can directly form a coating while polyelectrolyte multilayer films buildup process needs the alternation of positive and negative charge overcompensation, which possibly needs complementary species that has a risk in diluting the desired property of chosen species, especially in the area of conducting coatings. However, there are some limitations for PECs, one of them is the coating or film prepared by PECs is thin because of the repulsion from different PECs mixtures in a solution.

Electrophoretic deposition (EPD), a simple, cost effective and versatile method to fabricate coating or film, has currently gained widespread application starting from ceramics to advanced materials. In electrophoretic deposition, the charged powder particles suspended in a liquid are attracted and move towards the oppositely charged electrode where they eventually get deposited. Direct current (DC) electric field is widely used and organic liquids are generally used as the suspending medium because there is no water electrolysis occurred near the electrodes. However, organic solvents are hazardous and expensive which limits their application, therefore developing aqueous EPD has gained an increasing attention. In order to suppress water electrolysis, several
methods are applied, such as pulse DC\textsuperscript{113} and asymmetric alternating current (AC)\textsuperscript{114} etc.

In electrophoretic deposition, researchers have focused on studying ceramics but recently electrodeposition of polyelectrolytes are investigated, because they are environmental-friendly and easy to be tailored by controlling different variables (i.e. pH, concentration and ionic strength etc). PEMs fabricated via electric field assisted layer by layer technique has been widely studied\textsuperscript{115-117} and applying external electric field force to the LbL process has been proved that the electric field can enhance adsorption of polyelectrolytes and shorten the time required for preparing PEMs.\textsuperscript{117-118} However, the electrophoretic deposition of PECs, a new method with the potential to fabricate functional coatings or films, has not been studied.

In this work, polyelectrolyte complexes were fabricated by injecting polyacrylic acid (PAA) into branched polyethylenimine (BPEI) and controlled BPEI excessive. Under an electric field, positively charged BPEI/PAA complexes were deposited onto silicon wafer to form a thin film. According to Hamaker law, electrophoretic mobility is an affecting parameter in EPD process\textsuperscript{119}, therefore, electrophoretic mobility of BPEI/PAA complexes as function of ratio of BPEI and PAA was investigated and the highest mobility was obtained when the ratio of BPEI and PAA is 20. BEPI and PAA are both weak polyelectrolytes whose degree of ionization can be tailored by pH and the mobility of complex reached to a maximum value at pH 7.5. Moreover, BPEI/PAA complexes can be electro-deposited on a substrate under various types of electric field (i.e. pulsed DC at
constant potential, constant current, AC and continuous DC) with different electric field strength. In the EPD, water electrolysis was suppressed when a pulsed potential was used and the thickness of films increased with an increment of electric field strength while bubbles were formed on electrodes and a maximum thickness of film was gained at a moderate electric field strength when pulsed current was applied. NaCl can interact with BPEI/PAA complex by interacting with carboxylic groups in PAA. The relationship of BPEI/PAA complex mobility and concentration of NaCl was studied and enhanced mobility of BPEI/PAA complexes was obtained when a few amount of NaCl was added, resulting in a thicker film on the substrate.

3.2 Experimental section

Branched poly(ethylene imine) (BPEI, $M_w=25,000$ g/mol), poly(sodium 4-styrenesulfonate) (SPS, $M_w=70,000$ g/mol, powder), hydrochloric acid, sodium hydroxide, as well as poly(diallyldimethylammonium chloride) solution (PDAC, $M_w=400,000-500,000$ g/mol, 20 wt% aqueous solution) were purchased from Sigma-Aldrich. Poly(acrylic acid) (PAA, $M_w = 50,000$ g/mol, 25 wt% aqueous solution) was purchased from Polysciences, Alfa Aesar. DI water with 18.2 MΩ cm resistivity from a Milli-Q filtration system (Millipore, Bedford, MA, USA) was used for all experiments. All materials were used as received without further purification. BPEI aqueous solution with the concentration of 60 mM (respect to amine groups) and PAA aqueous solution with the concentration of 60 mM (respect to carboxylic acid groups)
were prepared by stirring overnight. Then, 1 M hydrochloric acid was used to adjust the pH of BPEI solution to 9.5 and 1 M sodium hydroxide was used to adjust the pH of PAA solution to 4.5. Both BPEI solution and PAA solution were filtered prior to use. PDAC and SPS aqueous solutions were prepared at concentrations of 15 mM (based on moles of repeating units) by stirring overnight and filtered before using.

3.2.1 Materials Fabrication

BPEI/PAA complexes were prepared by using syringe pump to inject PAA solution into BPEI solution with the ratio of BPEI and PAA of 20. The injecting rate was controlled at 15 mL/h. pH of BPEI/PAA complexes was adjusting by using 1 M hydrochloride acid to 7.5 and equilibrated for 20 min before being deposited onto a cleaned high conductive silicon wafer. The same procedure was used to prepare PDAC/SPS complexes.

For electrophoretic deposition, platinum gauze (25 x 25 mm) and highly conductive silicon wafer (10 x 20 mm) were used as electrodes and highly conductive silicon wafer was utilized as the deposition substrate (cathode).

Highly conductive silicon wafers were sequentially washed with methanol, acetone and deionized water for 15 min prior to deposition. The two electrodes were parallel to each other and the distance between the electrodes was controlled at around 1.5 cm. Different type of electric field with varied electric field strength was applied by a ZIVE SP1 electrochemical working station (WonATech Co. Seoul, Korea) and the field vector was perpendicular to the substrate. The deposition was carried out for 10 min and for
comparison purpose, deposition without applying electric field was also conducted for 10 min.

3.2.2 Characterization

The surface charge and electrophoretic mobility of BPEI/PAA complexes and PDAC/SPS complexes were analyzed by Zeta-potential Analyzer (Brookhaven Instrument, USA). The complexes were formed with different ratio of polycation and polyanion at varied pH.

Fourier transform infrared spectroscopy (FTIR) spectra were acquired by an Alpha-P FTIR spectrometer (Bruker Optics, Billerica, MA, USA) with attenuated total reflectance (ATR) mode. Samples were prepared by electrophoretic deposition of BPEI and BPEI/PAA complex onto highly conductive silicon wafers under a pulsed current at 10 mA for 10 min, respectively.

The thickness of PECs thin films was measured by using an ellipsometer (VASE, J.A. Woollam Co., Inc., Lincoln, NE, U.S.A.). The measurements were performed at three different angles (i.e. 65°, 70°, and 75°) and scanned across a wavelength range from 246 to 1689 nm. A four-layer model, which consists of a silicon substrate layer, a fixed 1.0 nm Si-SiO₂ interface layer, a 0.8 nm thermal oxide layer, and a Cauchy layer, which is an effective medium approximation layer (with thickness, A and B free fit parameters) in Complete EASE (J. A. Woollam, Co., Inc., Lincoln, NE, USA) was utilized to model the ellipsometric angles (Δ and Ψ), so the thickness of films can be determined.
To prove that electric field can enhance the deposition of polyelectrolytes, single polyelectrolyte BPEI was deposited on Q-Sense gold-coated quartz crystal sensor (QSX335). A Q-Sense E1 QCM-d instrument (Q-Sense, Gothenburg, Sweden) with Q-Sense electrochemistry module (QEM401) was applied to detect the response to the change of electric field. The crystal sensor as the working electrode was rinsed by DI water and dried overnight prior to the deposition of films and platinum plate was used as the counter electrode. BPEI was pumped to flow the cell at a flow rate of 50 μL/min and a continuous DC with constant current was applied. QCM-d data was processed via the commercial software package Q-Tools to calculate the change of mass on the substrate as a function of time.

3D zeta spectroscopy profilometer was utilized to observe the morphology of films prepared by single polyelectrolyte BPEI and BPEI/PAA complexes, respectively.

3.3 Results and discussion

Films made by BPEI/PAA complexes are prepared by the electrophoretic deposition as illustrated in scheme 6. BPEI films are also fabricated followed the same procedure.

After preparing BPEI/PAA complex solution, platinum mesh as the anode and silicon wafer as the cathode were parallel to each other and immersed into BPEI/PAA complex solution. Once applying an electric field, BPEI/PAA complexes carrying positive charges were forced to move along the direction of the electric field to the silicon wafer and deposited on the substrate to form a film.
After electrophoretic deposition, dry the film by using gentle pressed air. Since the film is thin, they cannot be peeled off from the substrate.

Scheme 6. Schematic illustration of the preparation process of BPEI/PAA complex and BPEI/PAA complex film via electrophoretic deposition.

Figure 16. The mass of BPEI increases on the substrate as function of time measured by QCM-d. A continuous DC with constant current of 1 mA/cm² was applied. The concentration and pH of BPEI was controlled at 60 mM and 7.0 respectively.

QCM-d is utilized to monitor the mass change on the substrate to indicate the deposition yield of BPEI. As shown in the Figure 16, BPEI with concentration of 60 mM is injected into the QCM cell and an initial increase in mass is observed. After 30 min, around
80 ng/cm$^2$ BPEI has been deposited onto the substrate. However, these BPEI are weakly bonded to the substrate and most of them are washed away on rinsing of DI water, illustrated by a reduction in the mass to 25 ng/cm$^2$ on the substrate. When an electric field with current density of 1 mA/cm$^2$ is applied to the cell, the adsorption of BPEI is enhanced and BPEI of around 230 ng/cm$^2$ is deposited on the substrate for 30 min compared with the deposition of less 100 ng/cm$^2$ BPEI without an electric field. After turning off the current, the amount of BPEI on the substrate is greatly decreased under the continuous flow of BPEI and 70 ng/cm$^2$ BPEI is remained on the substrate because of the weak interaction between BPEI and the substrate. The effect of the electric field on the deposition of BPEI can be repeatable. By turning on and off the electric field for four times, more than 200 ng/cm$^2$ BPEI can be deposited onto the substrate under an electric field and approximately 70 ng/cm$^2$ BPEI is left on the substrate once the electric field is turned down. The mass of BPEI on the substrate after finishing 4 cycles of applying an electric field is larger than one without applying electric field, which indicates the benefit of an electric field to enhance the deposition yield via inducing more positively charged BPEI to move towards to the oppositely charged electrode (gold-coated quartz crystal sensor) and triggering the deposition of BPEI.

The electric field strength, according to Hamaker law, is an affecting parameter in EPD process and the deposition yield is proportional to the electric filed. Whereas water electrolysis is promoted if the required decomposition potential ($\sim$1.3V) is applied,
resulting in oxygen and hydrogen released on electrodes and bubbles incorporated within films prepared on one of electrodes. Dinkelacker\textsuperscript{120} has investigated the current density and time for applying electric field required for the formation of bubbles. With lower current density and shorter time, bubble-forming precursors are easier to diffuse back to the bulk of the solution from electrodes and less possibility to form bubbles. By using pulsed potential and controlling the time for pulse ON time ($T_{\text{on}}$) and pulse OFF time ($T_{\text{off}}$), bubble formation can be suppressed and bubble-free deposits can be obtained.

Figure 17. (a) BPEI was deposited on the silicon wafer. The concentration was 200mM, and pH was 7.0. The potential was controlled 10V and time of applying potential was 0.5s, 0.05s and 0.01s from the left and right. The pulse OFF time was controlled at 1s and deposition time was 10min. The surface of BPEI with pulse ON time of 0.5s, 0.05s and 0.01s (b), (c), (d) was observed by an optical microscope.
Figure 17a shows images of BPEI films electrodeposited on substrates with different pulse ON time taken by a camera and from Figure 17b to Figure 17d, the surface morphology of BPEI films is observed by using an optical microscope. The pulse OFF time is kept constant while the pulse ON time is decreased from 0.5 s to 0.05 s to 0.01 s, less macro-bubbles are formed and no bubbles are seen by bare eyes when the pulse ON time is 0.01 s and surface of BPEI films becomes smoother, presented in a smooth and colorful surface.

The degree of ionization of BPEI, a weak polyelectrolyte, can be influenced by pH, the amine groups in BPEI can be protonated or deprotonated at an acidic or basic environment. The change of charge density imparts an impact on the electrophoretic deposition of BPEI. The thickness of BPEI deposits as a function of pH of BPEI is shown in Figure 18a.

![Graphs](image)

Figure 18. The thickness of BPEI films as function of pH (a) and potential (b). pH of BPEI solution was adjusted to 7.0. Pulsed potential was used with pulse ON time for 0.01 s and pulse OFF time for 1 s. Deposition time was 10 min.
After applying a pulsed potential at 10 V with pulse ON time and pulse OFF time of 0.01 s and 1 s, a thickest BPEI film is obtained with pH of BPEI 7.0 and the thickness decreases to ~110 nm at pH 10.0 and ~145 nm at pH 5.0. At a basic environment, the degree of ionization of BPEI is relatively low and thus less BPEI moves to the substrate under an electric field. By decreasing pH of BPEI, amine groups are protonated and BPEI carries more charges. With the same electric field strength, more BPEI molecules are driven towards the substrate. At pH 7.0, a BPEI film with the thickness of ~216 nm is prepared, which is two times thicker than one fabricated at pH 10.0. However, more charges on BPEI polymer chains requires less BPEI to deposit onto a substrate because of charge overcompensation.\textsuperscript{121} Also, an extension of BPEI polymer chains\textsuperscript{122} occurs at low pH, resulting in a thinner monolayer. In addition, stronger repulsion between BPEI molecules prevents sequentially adsorption of BPEI in the bulk solution when BPEI molecules are accumulated near the substrate and some of them has been deposited onto the substrate. Therefore, a decrease in the thickness of BPEI films is observed when pH is continuously decreased. At pH 5.0, the thickness of BPEI film is 145 nm, which is a little bit thicker than one prepared at pH 10.0.

The influence of electric field strength is investigated and results are shown in Figure 18b. The thickness of the film prepared by electrophoretically depositing 200 mM BPEI at a pulsed potential with a voltage of 2.0 V is ~40 nm larger than the film with thickness of ~160 nm fabricated by the deposition without an electric field. A continuous increment in
the thickness of BPEI films is correlated with increasing in electric field strength from 2.0 V to 10.0 V. The concentration of polyelectrolytes is another influencing parameter in determining the thickness of BPEI films. High concentration of BPEI (200 mM) causes thick films whose thickness is nearly 10 times higher than that of films made by BEPI with low concentration (60 mM) no matter if an electric field has been applied and what electric field strength is. Nevertheless, whatever the concentration of BPEI is, the relationship between thickness of BPEI films and electric field strength is the same. EPD includes two steps, one is to move charged particles to the substrate and the other is charged particles deposition due to a transition of particles from soluble to insoluble. For the second step, there are several mechanisms and one of them is change of local pH. Yoshio Sakka et.al\textsuperscript{123} has experimentally verified the pH localization mechanism. Near the electrodes, pH changes due to the water electrolysis. After applying an electric field, the environment is basic near the cathode and local pH near cathode/solution interface can attain plateau pH faster and get closer to the isoelectric point with a larger pulse width and higher electric field strength. However, a smaller pulse width is utilized in this study in order to obtain a film with an uniform surface morphology, so that the change of local pH is less significant, leading to a small change in the degree of ionization of BPEI. Although more BPEI can be transported to the substrate with an assistant of an electric field with an increasing electric field strength, no significant increase in the thickness of BPEI film under electric fields with different electric field strength can be observed.
Based on the study of single polyelectrolyte, the influence of different variables on electrophoretic deposition of BPEI/PAA complex has been investigated.

![Figure 19](image.png)

Figure 19. The picture of BPEI/PAA complex (a) and FTIR of BPEI film as well as BPEI/PAA complex film prepared by electrodeposition(b). BPEI solution and BPEI/PAA complex solution were subjected to a pulsed current at 10 mA with pulse ON time and pulse OFF time of 0.01s and 1s respectively. The concentration of BPEI/PAA complex was 60mM and pH was 7.5. The ratio of BPEI and PAA is 20:1.

In Figure 19a, the opaque rather than transparent solution indicates the formation of BPEI/PAA complex. It is well known that asymmetric stretching band of COO\(^-\) at \(\nu=1565-1542\ \text{cm}^{-1}\) and C=O stretching of COOH at \(\nu\approx1710\ \text{cm}^{-1}\) in the related FTIR spectra are characteristic adsorption bands of PAA,\(^{67}\) however, these two adsorption peaks are overlapped by adsorption peaks of BPEI because the content of PAA is much lower than that of BPEI, therefore there is no obvious difference between single BPEI films and BPEI/PAA complex films in FTIR spectra, shown in Figure 19b.

By using 3D zeta spectroscopy profilometer, the surface morphology of BPEI/PAA complex film comprises several particle-like structures, which is consistent with the theoretical structure of polyelectrolyte complexes brought about by Schlenoff et. al\(^{16}\),
while the surface of BPEI film is smooth, as shown in Figure 20a and 20b. The difference in surface morphology of films proves that BPEI/PAA complexes has been formed and deposited onto the substrate.

**Figure 20.** The picture of single BPEI (a) and BPEI/PAA complex (b) taken by 3D zeta spectroscopy profilometer. The concentration of single BPEI and BPEI/PAA complex were both 60mM and pH were both 7.5. A pulse current was applied. The current was 10mA and deposition time was 10min.

In EPD, many parameters regarding BPEI/PAA complex solution should be considered besides factors related to the electric field. Among several parameters, zeta potential and electrophoretic mobility are two important factors and the mobility depends linearly on the zeta potential by following Henry equation. Zeta potential of charged BPEI/PAA complex particles is imperative to achieve a highly surface-charged particles and it can determine the moving direction and migration velocity of charged particles under an electric field. During EPD, the stability of suspension is important and overall stability is governed by the sum of several forces (i.e. Van der Waals” force and electrostatic repulsion). A high zeta potential means a high electrostatic repulsion and repulsion of charged particles during deposition results in a film with high particle packing density.
otherwise a porous, sponge-like deposit is formed due to low repulsion and coagulation of particles.\(^{124}\) The zeta potential of BPEI/PAA complex can be controlled by different variables. One of them is the ratio of BPEI and PAA.

Figure 21. Zeta potential and mobility of complex changes as function of ratio of BPEI and PAA after adjusting pH of complex. pH of BPEI were 9.5 (a), 9.0 (b), 8.5 (c), 8.0 (d), 7.5 (e) and 7.0 (f). Zeta potential and mobility of complex as a function of pH of BPEI and ratio of BPEI and PAA was controlled at 20 (g). The concentration of BPEI and PAA were both 60 mM.
In Figure 21a, increasing the content of PAA while keeping pH of BPEI/PAA complex at 9.5 can achieve a highest zeta potential with the ratio of BPEI and PAA of 20:1. Meanwhile, highest mobility is also achieved since the mobility is calculated by using zeta potential. PAA can interact with BPEI and accumulate several BPEI polymer chains together to form a spherical structure. When large amount of PAA is injected to BPEI (ratio of BPEI and PAA is 5:1), positive charges of BPEI are compensated by negative charges of PAA. As a consequence, few net positive charges are remained and zeta potential of complex is low (~9.5 mV) and at the same time the mobility is only 0.7 ((u/s)/(V/cm)). By decreasing the content of PAA, more BPEI can exist in the solution and cover BPEI/PAA complex, making BPEI/PAA carry more positive charges. The zeta potential and mobility increase and reach the maximum values of 30.3 mV and 2.4((u/s)/(V/cm)) respectively at the ratio of BPEI and PAA of 20:1. However, when few PAA is added into BPEI solution and BPEI is greatly excess, the suspension is more like BPEI solution rather than BPEI/PAA complex solution. A single polyelectrolyte polymer chain has limited zeta potential and mobility, therefore a low zeta potential and mobility (14 mV and 1.1 ((u/s)/(V/cm)) respectively) are shown with extremely low ratio of BPEI and PAA of 50:1. Similar trend between zeta potential and ratio of BPEI and PAA can be seen from Figure 21b to 21f at different pH of BPEI/PAA complex, which is another important factor determining the zeta potential and mobility of BPEI/PAA complex. BPEI and PAA in this study are both weak polyelectrolyte and their degree of ionization is dependent on pH of the solution. At high pH, BPEI is less charged while PAA carries
more charges, by decreasing pH from 9.5 to 7.0, BPEI carries more positive charges while PAA is less charged,\textsuperscript{65} during this process, density of crosslink within BPEI/PAA complexes will achieve the maximum when degree of ionization of both BPEI and PAA are proper. In Figure 21g, zeta potential and mobility increases to \( \sim 53 \text{ mV} \) and \( \sim 4.1 \text{ ((u/s)/(V/cm))} \) at pH 7.5, which is about two times larger than those of BPEI/PAA complex at pH 9.5, and both of them decrease to \( \sim 45 \text{ mV} \) and \( \sim 3.5 \text{ ((u/s)/(V/cm))} \) when pH is 7.0 due to a weak interaction between BPEI and PAA. Therefore, BPEI/PAA complex at pH 7.5 and ratio of BPEI and PAA of 20:1 is applied in the following experiments to study important factors related to the electric field.

Figure 22. The thickness of BPEI/PAA films changes as a function of potential (a) and current (b). The pH of BPEI/PAA complex was controlled at 7.5. The ratio of BPEI and PAA was 20:1. Pulsed potential and pulsed current were both used with pulse ON time of 0.01s and pulse OFF time of 1s. Deposition time was 10min.

Pulsed EPD was investigated at both constant voltage and constant current mode. In Figure 22a, traditional deposition of BPEI/PAA complexes without an electric field forms a film with thickness of 23 nm while the deposition of BPEI achieve a film with
thickness of 19 nm (Figure 18b), which is consistent with lower mobility of BPEI compared with that of BPEI/PAA complexes. The formation of macro-scaled bubbles is suppressed upon applying pulsed potential with a short pulse ON time, and the change of local pH near electrodes is not significant, therefore thickness of films made by BPEI/PAA complex increases from 29 nm to 47 nm due to an increment of electric field strength. The limitation of applying pulsed potential is the voltage distribution caused by the resistance of substrate. Voltage on a point of the substrate far from the power supply is lower than that located near the power supply, causing a gradient of voltage on the substrate. Therefore, pulsed current was utilized to overcome this limitation. In Figure 22b, the influence of electric field strength on the thickness of BPEI/PAA complex films is investigated by raising current. Macro-bubbles are formed with using the same length of pulse ON time and pulse OFF time as those in applying pulsed potential and the increase of local pH near electrodes is expected to be more evident compared to use pulsed potential. After applying an pulsed current of 1 mA, the adsorption of BPEI/PAA complex is greatly enhanced and the thickness is more than 2 times larger than that of films fabricated without an electric field, as a consequence of enhanced mass transport of BPEI/PAA complex and neutralization of positively charged BPEI/PAA complexes in a basic environment near the substrate. The thickness increases to ~63 nm at current 10mA but reduces to ~31 nm at current 100 mA. This change is due to the pH dependent ionization of both BPEI and PAA. BPEI and PAA are both partially charged with a moderate ionic crosslink density within BPEI/PAA complexes. In the electrodeposition,
pH at the substrate-solution interface is raised with consuming protons by reduction occurred on the cathode. A moderate increase in pH can compensate surface charges of BPEI/PAA complexes and trigger coagulation of BPEI/PAA complex to enhance the deposition, while BPEI/PAA complexes are partially dissolved under an extremely basic environment caused by high electric field strength, such as pulsed current of 50 mA or 100 mA, giving rise to a decrease in the thickness of films.

![Graphs showing the thickness of BPEI/PAA complex films as a function of pulse width, duty cycle, and electric field.](image)

**Duty cycle (%) = \( \frac{\text{pulseON}}{\text{pulseOFF}} \)**

Figure 23. The thickness of BPEI/PAA complex films as a function of pulse width (a), duty cycle (b). For pulse width, pulse ON and OFF time was changed simultaneously and duty cycle was controlled at 50%. The current was 10 mA. The thickness of films as a function of duty cycle, AC mode was applied (c). The ratio of BPEI and PAA was 20:1. The deposition time was 10 min. The concentration and pH of complex was 60 mM and 7.5.

Figure 23 shows the electrophoretic deposition of BPEI/PAA complexes under different types of electric field. Pulsed EPD experiments were conducted by using constant current mode with different pulse width and duty cycle. A typical current pulse wave with 50%
duty cycle was applied and pulse width was varied by simultaneously changing pulse ON time and pulse OFF time. The corresponding thickness of films is shown in Figure 23a. The maximum deposition occurs on applying a pulsed current with the pulse width of 0.01 s and the yield decreases to ~65 nm and ~55 nm at low pulse width 0.005 s and high pulse width 0.1 s. Moreover, the film becomes thinner to ~50 nm on application of continuous DC. Similar trend of higher deposition yield with a moderate duty cycle and lower deposition yield with low duty cycle and high duty cycle is observed at an applied pulsed current with different duty cycles (Figure 23b). Applying the electric field with 10% duty cycle and 90% duty cycle turns into thinner films with the thickness of 48 nm and 70 nm, in contrast with a 80 nm film when BPEI/PAA complexes are subjected to an electric field with 70% duty cycle. During pulsed EPD, BPEI/PAA complexes can be continually transported from bulk suspension to the substrate during the pulse OFF time due to their inertia of mobility induced by the influence of preceding pulse ON duration. With low pulse width or duty cycle, there is shorter pulse ON time, as a consequence, the influence of pulse ON period on the inertial of mobility is less significant and less mass transport of BPEI/PAA complexes is achieved and thinner films are obtained. On the other hand, Yoshio Sakka et. al has experimentally prove that high pulse width or duty cycle can induce more macro-bubbles compared with low pulse width or duty cycle, resulting in a more dramatic change in local pH near electrodes. At extreme pH, BPEI/PAA complexes are dissolved and the thickness decreases. In addition, more bubbles are formed and incorporated within films, the surface becomes rougher,
which can be indicated by larger error bars at high pulse width or duty cycle (Figure 23a and Figure 23b). AC square wave with various duty cycle is investigated in Figure 23c. A maximum thickness of ~86 nm is obtained with duty cycle of 80% and the thickness diminishes to ~54 nm and ~56 nm at duty cycle 50% and 90%, respectively. An asymmetric AC square wave should be utilized to induce BPEI/PAA complexes have a net motion toward the cathode despite the alternation of electric field direction during deposition. However, Peyman Servati et. al\textsuperscript{125} has successfully deposited cobalt nanowires onto porous anodized aluminum oxide substrate by using symmetric AC square wave, which is consistent with the result in our study. The deposition of BPEI/PAA complex under AC mode with 50 % duty cycle is enhanced compare to deposition without electric field because of inertia mobility of BPEI/PAA complexes induced by preceding positive direction of electric field and short distance between two electrodes. Electrochemical decomposition of water causes pH to increase near the substrate worked as cathode and decrease once the substrate works as anode. In our study, an asymmetric AC square wave is applied, the pH thus tends to be basic near the substrate as result of the existence of more protons than hydroxyl ions except of AC mode with duty cycle of 50%. Increasing pH will lead to a neutralization of BPEI/PAA complexes so that they can accumulate on the substrate without electrical repulsion. Again, BPEI/PAA complexes will be dissolved when pH near the substrate increases beyond a certain value, which will make the thickness of BPEI/PAA complex films decrease. By using AC mode, it can also have a function of suppressing the formation of
macro-bubbles to some extent. By comparing to pulsed current with different pulse width and duty cycle (Figure 23a and 23b), AC can induce a smoother surface of BPEI/PAA complex films, indicated by smaller error bars of the thickness.

To prove that the trend of thickness of films is correlated with the local pH near electrodes, a strong polyelectrolyte complex pair PDAC/SPS whose degree of ionization is independent on pH, is electrophoretically deposited onto the substrate. Zeta potential and mobility of PDAC/SPS complex is also investigated and the highest zeta potential and mobility are achieved with the ratio of PDAC and SPS of 20:1, shown in Figure 24a.

![Figure 24. Zeta potential and mobility of PDAC/SPS complex as a function of ratio of PDAC and SPS (a). The thickness of PDAC/SPS complex films as a function of duty cycle under AC mode with constant current of 10 mA (b). The concentration of complex was 15 mM and the ratio of PDAC and SPS was 20:1. The deposition time was 10 min.](image)

Under AC square wave, the deposition of PDAC/SPS complex is enhanced. Compare to films prepared by traditional deposition for 10 min, films become thicker and thickness is increased to 64 nm in spite of applying AC mode with duty cycle 50% (Figure 24b).
Increasing duty cycle turns into an increase in the thickness of films and the thicker film with 96 nm is obtained under a continuous DC with constant current of 10 mA.

This trend is different with that shown in electrophoretic deposition of weak polyelectrolytes BPEI/PAA complex. Electrophoretic deposition of PDAC/SPS complex can be explained by a theory of electrical double layer distortion, brought by Sarkar et.al.\textsuperscript{124} PDAC/SPS complex with excessive PDAC molecules carries positive charges and they are surrounded by counterions to form an electrical double layer. Under an electric field, electrical double layer will distort and become thinner ahead while wider behind the PDAC/SPS complex molecules. PDAC/SPS complexes along with ions of similar charge move to the substrate and these coions will interact with counterions surrounding PDAC/SPS complex to make double layer thinner, leading to a coagulation and deposition under Van der Waals attractive force between different PDAC/SPS complex molecules. Since the local pH will not influence the degree of ionization of PDAC and SPS, with increasing duty cycle, there is more time for the electric field with positive direction so that more PDAC/SPS complexes can be transported to the substrate and deposited onto it without consideration of dissolution of polyelectrolyte complex at extreme pH.

In EPD, the concentration of electrolyte is another affecting factor. Also, the charge density of polyelectrolytes can be modulated by the ionic strength. Based on this effect, the content of salt can strongly influence the properties of polyelectrolytes. Therefore, the
mobility of BPEI/PAA complex with different concentration of salt with varied equilibrate time was investigated. The corresponding results are shown from Figure 25a to Figure 25d.

Figure 25. The mobility of BPEI/PAA complexes as a function of equilibrating time. The concentration of NaCl is 0 mM (a), 1 mM (b), 5 mM (c) and 10mM (d). The concentration and pH of BPEI/PAA complexes were 60 mM and 7.5. The ratio of BPEI and PAA was controlled at 20:1.

Without adding salt into polyelectrolyte complexes, the solution is stable regardless of equilibrate time and the mobility is around 3.6 ((u/s)/(V/cm)). After adding salt into BPEI/PAA complexes, the mobility changes with elongating equilibrate time. In Figure 25b, the mobility of BPEI/PAA complex with 1 mM NaCl increases from 3.4 ((u/s)/(V/cm)) to ~3.8 ((u/s)/(V/cm)) after equilibrating for 30 min while decreases to
When one hour passes, similar trend can also be observed with other concentration of salt. However, adding 10 mM salt into BPEI/PAA complexes makes the solution change from turbid to clear after equilibrating for 20 min, indicating the dissolution of BPEI/PAA complexes. Salt can interact with carboxyl groups in PAA and amine groups in BPEI and decrease the surface charges of BPEI/PAA complexes, as a result, BPEI/PAA complexes can coagulate so that BPEI/PAA complexes are possible to have more charges on the surface, in addition, bringing salt into polyelectrolyte complexes can also contribute to the mobility of the solution, hence the overall charges and mobility of BPEI/PAA complexes increase. As shown in Figure 25b, the mobility increases after 30 min. Nevertheless, salts can break the crosslinks within polyelectrolyte complexes because of charge screening effect and the mobility of the solution decreases. This process needs time. With time consuming, the bonds between BPEI and PAA gradually break and BPEI/PAA complexes are dissolved, so the mobility of the solution decreases after 1 h. A high concentration of salt (10 mM in this study) has stronger charge screening effect and the time for breaking crosslinks within BPEI/PAA complexes is shorter, hence the mobility has a low value of 3.1 ((u/s)/(V/cm)) compared to that of the solution with 1mM salt, which proves that the mobility can be enhanced by adding proper concentration of salt (Figure 26a). The corresponding thickness of films prepared by using BPEI/PAA complexes with different concentration of salt is shown in Figure 26b. The thickness increases from 63 nm to 74 nm after adding 1 mM NaCl into BPEI/PAA complexes but significantly decreases to 25 nm with 10 mM NaCl in
BPEI/PAA complexes. This result further demonstrates a proportional relationship between the mobility of BPEI/PAA complex solution and deposition yields.

Figure 26. (a) The mobility of BPEI/PAA complex as a function of concentration of NaCl. The thickness of BPEI/PAA complex films as a function of concentration of NaCl (b). The concentration of BPEI and PAA are both 60mM and pH of complex is 7.5. The pulsed current with pulse ON time of 0.01 s and pulse OFF time of 1s was applied and deposition time was 10min. Current was controlled at 10mA.

3.4 Conclusion

BPEI/PAA complexes as a new method have a potential to prepare functional films and electric field can enhance the deposition of BPEI/PAA complexes and overcome the limitation of low deposition yields of polyelectrolyte complexes due to the repulsion between polyelectrolyte complexes. In EPD using aqueous solution, water electrolysis occurs, resulting in the formation of bubbles when the potential reaches beyond a certain value and pulsed EPD with controlled pulse ON time and pulse OFF time can suppress the bubbles formation. Polycation (BPEI) with different pH values are electrophoretically deposited onto the substrate under a pulsed potential and highest
deposition yield is achieved at pH 7.0. By increasing the electric strength, the deposition yield is enhanced because more BPEI carrying positive charges are transported to the substrate and deposited onto substrate when they are neutralized at a locally basic environment near the substrate. Injecting PAA into BPEI forms BPEI/PAA complexes and zeta potential as well as mobility of BPEI/PAA complexes are modulated by the ratio of BPEI and PAA and pH of complexes as well. Changing these two parameters of BPEI/PAA complexes will tailor the charge density of BPEI/PAA complexes and lead to a varied mobility. The change in the thickness of films made by BPEI/PAA complexes is corresponding to the mobility of BPEI/PAA complexes despite the same type of electric field with same electric field strength. Regardless of type of electric field, the thickness of films made by BPEI/PAA complex achieves a maximum value at a moderate electric field strength while decreases when BPEI/PAA complexes are subjected to a high electric field strength because of the dissolution of BPEI/PAA complexes at a basic environment near the substrate, while a proportional relationship between the thickness of films and electric field strength is observed when PDAC/SPS complexes are used. Therefore, the local pH near the substrate is also an affecting factor in the deposition yield besides of electric field strength. Moreover, adding salt can affect the charge density and break the crosslinks within BPEI/PAA polyelectrolyte complexes, causing a change in the mobility and resulting in an increment in the deposition yield with a small amount of salt but a decrease in the deposition yield with adding a high concentration of salt into BPEI/PAA complexes.
CHAPTER IV

CONCLUSION AND FUTURE WORK

In this study, we have developed BPEI/PAA multilayer films as wet adhesive materials which are capable of adhering to various substrates. The adhesive property of BPEI/PAA multilayer films under different variables has been investigated. It has been observed that the interactions between different metal ions and BPEI/PAA multilayer films are complicated, creating a more adhesive material when films are wetted by transitional metal ions in most cases, while reducing adhesive nature on applying alkali metal ions. The adhesive behavior of films exposed to Cu$^{2+}$ ions are mainly studied and the film becomes stiff and solid-like and rheological data demonstrate the change of the physical properties of films wetted by Cu$^{2+}$ ions. Another part of this study focuses on the electrodeposition. We have investigated the variables that have an influence on polyelectrolyte thin film formation via electrodeposition by using polycation solution (BPEI) and suppressed bubbles formation by utilizing a pulsed potential with small pulse width. Moreover, we have deposited films made from BPEI/PAA complexes under different types of electric field (i.e. pulsed potential, pulsed current and AC mode) with determined electric field strength and studied the influence of these factors on the thickness of BPEI/PAA complex films, giving a pathway to fabricate a functional films by using a different method than the standard sequential depositing steps. In the future, other type of metal ions including alkali metal ions and transitional metal ions will be
added into polyelectrolyte complexes since they can interact with the polyelectrolyte complexes, modulating the zeta potential as well as the mobility of polyelectrolyte complexes. Moreover, an electric field can induce the orientation of charged particles or polymer chains, hence the orientation within polyelectrolyte complex films prepared by the electrophoretic deposition should be further investigated. In our study, we have focused on depositing polyelectrolyte complexes onto a substrate worked as one of electrodes. In future work, the electrophoretic deposition of polyelectrolyte complexes on a substrate located between electrodes should be investigated. This method can produce a smoother surface and has a potential in application of preparing separation membranes.
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