SELF-HEALING MECHANISM AND APPLICATION OF
ACRYLIC MATERIALS

A Thesis Submitted to the College of
Graduate Studies and Research
In Partial Fulfillment of the Requirements
For the Degree of Doctor of Philosophy
In the Department of Mechanical Engineering
University of Saskatchewan

Saskatoon

By

Fan Fan

© Copyright Fan Fan, December, 2016. All rights reserved.
PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a postgraduate degree from the University of Saskatchewan, I agree that the Libraries of this University may make it freely available for inspection. I further agree that permission for copying of this thesis in any manner, in whole or in part, for scholarly purposes may be granted by the professor who supervised my thesis work or, in their absence, by the Head of the Department or the Dean of the College in which my thesis work was done. It is understood that any copying or publication or use of this thesis or parts thereof for financial gain shall not be allowed without my written permission. It is also understood that due recognition shall be given to me and to the University of Saskatchewan in any scholarly use which may be made of any material in my thesis.

Requests for permission to copy or to make other use of material in this thesis in whole or part should be addressed to:

Head of the Department of Mechanical Engineering

57 Campus Dr.

University of Saskatchewan

Saskatoon, Saskatchewan (S7N 5A9)
ABSTRACT

Self-healing materials have attracted significant attention from researchers during last decades. However, self-healing materials cannot find practical applications yet due to a weak mechanical strength. Recently, it was identified that an acrylic elastomer, VHB 4910, has an excellent self-healing ability accompanied with a good mechanical strength. This material has been used to fabricate artificial muscles because it has unique dielectric properties.

Our study demonstrated that VHB 4910 has a self-healing ability. The self-recovery and self-healing ability of this material after separation by cutting was tested by unidirectional and cyclic tensile tests. It was demonstrated that the strength can be completely recovered or even improved when an elevated temperature is used to accelerate the healing process. The self-healing mechanism was also analyzed by recording the Raman spectra at different distances from the cut and at various times. Analysis of Raman spectra and X-ray diffraction experiments were used to generate a support for the proposed model of self-healing. According to this model the self-healing mechanism of the acrylic elastomer can be attributed to the synergistic effect of the re-association of hydrogen bonding and the diffusion of molecular chains.

Furthermore, another application of self-healing materials was proposed in this research. The coating that has not only the self-healing ability but also highly improved corrosion resistance was developed. In this research, a self-healing anticorrosion coating via layer-by-layer (LbL) assembly of the poly(acrylic acid) and poly(ethylene imine) was prepared on the magnesium alloys and electrogalvanized steel (EGS). This coating exhibits a rapid self-healing ability in the presence of water. The self-healing ability can be attributed to the swelling behavior of the damaged area of the coating. In the healing process, water played a role of plasticizer and allowed to increase the mobility of the molecular chains in the polyelectrolyte coating. When graphene oxide (GO) was added into the multilayer coating the corrosion resistance improved by two orders compared to the bare magnesium alloy. The GO layer acts as a strong barrier against the penetration of the corrosive electrolytes and provides an extended corrosion protection to the substrate. Therefore, the proposed multilayer coating with the addition of GO has a rapid self-healing ability and an excellent corrosion resistance.
ACKNOWLEDGEMENTS

First of all, I would like to appreciate China Scholarship Council (CSC) for their generous sponsorship for my living expenses in Canada during last 4 years.

I would like to thank my committee members, Prof. Torvi, Prof. Szyszkowski, Prof. Boulfiza, Prof. Meda and Prof. Guo. You showed your expertise during all my committee meeting by which I received many useful comments on my project. These comments did help me improve my research.

I would like to express my many thanks to all the colleagues who helped me during last four years. I still remember the first time when I got a chance to operate the SEM and XRD machine. It is Siyamak and Hamed who instructed me with their most patience. I won’t forget the time with Lina, Ming, Xu and Chunyu when we discussed our research and shared our ideas. It is the brainstorm we experienced that stimulated and promoted my research.

I also appreciate our department assistant, Mr. Rob Peace, who provided a lot of help at the beginning of my arrival. The whole laboratory including the rules and the facilities were new to me. It is his extremely patience and kind assistance that helped me survive and progress.

Finally, I want to give my most respect and appreciation to my supervisor, Prof. Szpunar. I really appreciate Prof. Szpunar who accepted my application and gave me the chance to study in such a beautiful university. It is not easy to adapt to a new lifestyle which I have never experienced before, not to mention the research transition from mechanical manufacture to materials science. It is the trust from Prof. Szpunar that helped me successfully catch up the studying rhythm and narrow my knowledge gap.
DEDICATION

This thesis is dedicated to my wife and my parents without whom it cannot be completed.
TABLE OF CONTENTS

PERMISSION TO USE........................................................................................................... i
ABSTRACT.................................................................................................................................. ii
ACKNOWLEDGEMENTS ........................................................................................................ iii
DEDICATION.......................................................................................................................... iv
TABLE OF CONTENTS............................................................................................................ v
LIST OF TABLES.................................................................................................................... x
LIST OF FIGURES.................................................................................................................. xi
ACRONYMS........................................................................................................................... xvi

1. Introduction......................................................................................................................... 1
   1.1. Background of self-healing.......................................................................................... 1
   1.2. Motivations ............................................................................................................... 2
       1.2.1. The self-healing acrylic elastomer VHB 4910................................................... 2
       1.2.2. The importance to protect magnesium alloys.................................................... 3
       1.2.3. Addition of graphene oxide ............................................................................. 3
       1.3. Objectives ............................................................................................................. 4

2. Literature Review ............................................................................................................... 7
   2.1. Overview .................................................................................................................... 7
   2.2. The mechanism of self-healing materials ................................................................. 8
       2.2.1. Hydrogen bonding ......................................................................................... 8
       2.2.2. Hydrophobic interactions ............................................................................. 9
       2.2.3. Electrostatic attractions ............................................................................... 11
       2.2.4. Reversible covalent bonding .................................................................... 12
       2.2.5. Encapsulated healing agent .................................................................. 13
   2.3. The application of self-healing materials ................................................................. 14
2.3.1. Self-healing anticorrosion coating ............................................................................. 14
2.3.2. Self-healing superhydrophobic coating .................................................................... 16
2.3.3. Self-healing barrier membranes .............................................................................. 17
2.4. Summary .................................................................................................................... 18

3. Experimental Methodology .......................................................................................... 20

3.1. Overview ...................................................................................................................... 20
3.2. The deformation mechanism behind the tensile tests of acrylic elastomer ............. 21
    3.2.1. The entropic contribution to the elastomer deformation ........................................ 21
    3.2.2. The energetic contribution to the elastomer deformation ......................................... 23
    3.2.3. The experimental setup .......................................................................................... 23
3.3. The assembly mechanism of layer-by-layer (LbL) technique .................................... 24
    3.3.1. The growth mechanism of LbL assembly of polyelectrolytes ............................... 24
    3.3.2. The thermodynamic aspect of LbL assembly of polyelectrolytes ............................ 26
    3.3.3. The experimental setup .......................................................................................... 27
3.4. The analysis of corrosion mechanism by electrochemical impedance spectroscopy (EIS) 28
    3.4.1. The electrochemical aspect of corrosion ................................................................. 28
    3.4.2. The basics of EIS .................................................................................................... 29
    3.4.3. The experimental setup .......................................................................................... 33
3.5. The working mechanisms of other characterization techniques ............................... 33
    3.5.1. X-ray diffraction (XRD) ......................................................................................... 33
    3.5.2. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)
    ........................................................................................................................................ 34
    3.5.3. Raman spectroscopy ............................................................................................. 34
3.6. Summary ...................................................................................................................... 36

4. The characterization and self-recovery behavior of acrylic elastomer VHB4910 .......... 38
4.1. Overview .......................................................................................................................... 38

4.2. The characterization of the acrylic elastomer ................................................................. 39

4.2.1. The chemical structure of the acrylic elastomer ....................................................... 39

4.2.2. The tensile behavior of the acrylic elastomer ......................................................... 42

4.2.3. The deformation speed effect on the tensile tests ..................................................... 44

4.2.4. The hysteresis behavior of the acrylic elastomer ..................................................... 46

4.3. The self-recovery behavior of the acrylic elastomer ..................................................... 48

4.3.1. The strain dependence of self-recovery ability ......................................................... 48

4.3.2. The time dependence of self-recovery ability .......................................................... 50

4.4. Summary ........................................................................................................................ 52

5. The self-healing behavior and mechanism of acrylic elastomer VHB 4910 .............. 54

5.1. Overview ........................................................................................................................ 54

5.2. Characterization of the self-healing behavior ............................................................... 55

5.2.1. The tensile test setup ............................................................................................... 55

5.2.2. The time-dependent self-healing ability ................................................................... 55

5.3. Determination of the self-healing mechanism ............................................................... 59

5.3.1. The role of hydrogen bonding in self-healing ......................................................... 60

5.3.2. The chain diffusion effect on self-healing .............................................................. 65

5.4. Summary ........................................................................................................................ 70

6. The poly(ethylene imine)/poly(acrylic acid) (PEI/PAA) multilayers self-healing coating on magnesium alloy AZ31 ................................................................. 72

6.1. Overview ........................................................................................................................ 72

6.2. Preparation and characterization of the PEI/PAA multilayers coating ....................... 73

6.2.1. Preparation of the cerium conversion layer ............................................................ 73

6.2.2. Preparation of the PEI/PAA multilayers ................................................................. 74
6.2.3. Characterization of the PEI/PAA multilayers ........................................................................ 77
6.3. The corrosion resistance of the PEI/PAA multilayers coating .................................................... 77
  6.3.1. The EIS results of the PEI/PAA multilayers ........................................................................ 77
  6.3.2. The buffering effect of the PEI/PAA multilayers .................................................................. 80
6.4. The self-healing behavior and mechanism of the PEI/PAA multilayers ................................. 83
  6.4.1. The self-healing behavior of the PEI/PAA multilayers .......................................................... 83
  6.4.2. The self-healing mechanism of the PEI/PAA multilayers .................................................... 85
6.5. Summary ...................................................................................................................................... 88

7. The graphene oxide (GO) incorporated PEI/PAA multilayers self-healing coating on magnesium alloy AZ31 ............................................................................................................. 90
  7.1. Overview .................................................................................................................................. 90
  7.2. Preparation and characterization of the multilayer coating ....................................................... 91
    7.2.1. Preparation of the multilayer coating ................................................................................. 91
    7.2.2. Characterization of the multilayer coating ....................................................................... 93
  7.3. The self-healing behavior of the multilayer coating ................................................................. 97
  7.4. The corrosion resistance of the multilayer coating .................................................................. 98
    7.4.1. The EIS results of the multilayer coating ........................................................................... 98
    7.4.2. The polarization resistance and protection efficiency of the multilayer coating .......................... 106
  7.5. The degradation process and protection mechanism of the multilayer coating ..................... 108
    7.5.1. The degradation process of the multilayer coating ............................................................... 108
    7.5.2. The protection mechanism of the multilayer coating ......................................................... 114
  7.6. Summary .................................................................................................................................. 118

8. The application of PEI/PAA multilayers self-healing coating on electrogalvanized steel ................................. 119
  8.1. Overview ................................................................................................................................... 119
  8.2. Preparation and characterization of the PEI/PAA multilayers coating on EGS ........................ 120
8.3. The self-healing behavior of the PEI/PAA multilayers coating on EGS.......................... 123
8.4. The corrosion resistance of the PEI/PAA multilayers coating on EGS......................... 124
8.5. The analysis of the corrosion products on bare EGS and (PEI/PAA)20 ....................... 133
8.6. The degrading process of bare EGS and (PEI/PAA)20 ........................................ 141
8.7. Summary ............................................................................................................. 143

9. Conclusions and future work .................................................................................. 144

9.1. Summary and Conclusions ................................................................................ 144
9.2. Contributions to original knowledge ................................................................. 146
9.3. Future works ....................................................................................................... 147

10. References ........................................................................................................... 148

11. Appendix .............................................................................................................. 169
LIST OF TABLES

Table 4.1 Observed wavenumbers and assignment of Raman and FTIR bands.................. 41
Table 7.1 Fitted EIS data for bare AZ31, Ce(IV)/GO/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 ................................................................. 105
Table 8.1 Fitted EIS data for bare EGS and (PEI/PAA)20............................................. 132
Table 8.2 EDS results for bare EGS and (PEI/PAA)20 after 72h EIS tests ......................... 135
Table 8.3 The Raman bands assignment of bare EGS and (PEI/PAA)20 after 72 h EIS tests... 140
LIST OF FIGURES

Figure 3.1 The intrinsic and extrinsic compensation of LbL assembly ........................................... 25
Figure 3.2 The thermodynamics of LbL assembly ............................................................................ 27
Figure 3.3 The example of (a) Nyquist plots and (b) Bode diagrams .................................................. 31
Figure 3.4 The example of equivalent models for a coated sample ..................................................... 32
Figure 3.5 The comparison of Rayleigh scattering and Raman scattering ........................................ 36
Figure 4.1 Identification of the chemical bonds in VHB 4910. (a) The Raman spectrum. (b) The FTIR spectrum ........................................................................................................................................ 37
Figure 4.2 The XRD pattern of VHB 4910 ......................................................................................... 40
Figure 4.3 The tensile test of VHB 4910. (a) The strain-stress curve under a deformation speed of 100 mm/min. (b) The modulus and the division of the strain-stress curve ...................................................... 41
Figure 4.4 The strain-stress curves under different deformation speed ................................................ 42
Figure 4.5 The deformation speed dependency of the shear modulus of crosslinked networks (Gx) and the shear modulus of entangled networks (Ge) .............................................................................................................. 43
Figure 4.6 Analysis of the hysteresis behavior of VHB 4910. (a) The hysteresis area increases with the tensile strain. (b) The hysteresis area and the energy dissipation ratio shown as a function of the tensile strain .................................................................................................................................. 44
Figure 4.7 The dissociation fraction and recovery efficiency as a function of the tensile strain ........ 45
Figure 4.8 Measurement of the self-recovery ability of VHB 4910. (a) The two hysteresis loops between 60 min of two cyclic test at a strain of 2 mm/mm and 8 mm/mm, respectively. (b) The self-recovery ability decreased with the increase of tensile strains ........................................................................................................................ 46
Figure 4.9 The time dependency of self-recovery ability. (a) The hysteresis recovered after 0.25 min. (b) The hysteresis recovered after 1 min. (c) The hysteresis recovered after 5 min. (d) The hysteresis recovered after 30 min. (e) The hysteresis recovered after 60 min. (f) The hysteresis recovered after 120 min ............................................................................................................................................. 47
Figure 5.1 The self-healing experiment of VHB 4910. (a) The sample was cut in the center and brought together manually. (b) The healed sample before and during a tensile test .................................................................................................................. 48
Figure 5.2 The self-healing test results under room temperature. (a) The fracture strain and stress increase with the healing time. (b) The best healed sample under room temperature. (b) The self-healing efficiency increases with the healing time ........................................................................................................ 49
Figure 5.3 The comparison of the fracture strain and stress with and without a waiting time of 40 hours................................................................................................................................................................................................. 59
Figure 5.4 The Raman spectrum of the carbonyl bands along a scanning line perpendicular to the cutting interfaces........................................................................................................................................................................................................................................ 60
Figure 5.5 The analysis of the Raman spectrum. (a) The 2nd derivation of the Raman spectrum of the carbonyl bands. (b) The Lorentz fitting of the Raman spectrum of the carbonyl bands. ...... 61
Figure 5.6 The variation of the carbonyl bands with respect to the distance from the cutting interfaces. (a) The change of wavenumber and FWHM of the hydrogen bonded carbonyl bonds with the distance from the cutting interfaces. (b) The change of the wavenumber and FWHM of the free hydrogen bonded carbonyl bonds with the distance from the cutting interfaces. (c) The Raman intensity and intensity ratio of the two carbonyl bonds change with the distance from the cutting interfaces........................................................................................................................................................................................................................................................................... 63
Figure 5.7 The comparison of the fracture strain and stress with and without the urea treatment after a healing time of 30 minutes........................................................................................................ 64
Figure 5.8 The proportional relationship between the true fracture stress of healed samples and the healing time in double-logarithm coordinates................................................................. 66
Figure 5.9 The Raman spectra of the carbonyl bands with different healing time. (a) The Raman spectra of the carbonyl bands at the cutting interfaces with different healing times. (b) The Raman intensity increases with the healing time. (c) The Raman spectra of the carbonyl bands at a pristine spot.................................................................................................................................................................................................................................................................................................................. 68
Figure 5.10 The effect of temperature on the healing behavior. (a) The strain-stress curve of healed samples with different healing temperature. (b) The fracture strain and stress increase with the healing temperature. (c) The healing efficiency increases with the healing temperature............. 69
Figure 5.11 The scheme of the self-healing mechanism of the acrylic elastomer......................................................... 70
Figure 6.1 The SEM images of the cerium conversion layers. (a) The bare AZ31 polished with #1200 SiC paper. (b) The cerium conversion layer after immersion in 0.05 M cerium nitrate for 20 min. (c) The cerium conversion layer after immersion in 0.05 M cerium nitrate for 30 min. (d) The cerium conversion layer after immersion in 0.05 M cerium nitrate for 30 min and sintered at 80 degrees Celsius for 30min................................................................................................................................................................................................................................................................................................................................. 74
Figure 6.2 The multilayer structure of the multilayers coating .................................................................................. 75
Figure 6.3 The XRD pattern and Raman spectra of the multilayer coatings. (a) The XRD pattern. (b) The Raman spectra. ........................................... 76

Figure 6.4 The EIS results of the multilayer coatings. (a) The Bode phase results. (b) The Bode impedance results. (c) The Nyquist plot results. .................................................. 79

Figure 6.5 The salt immersion tests of the multilayer coatings ............................................. 81

Figure 6.6 The cross-section images of the cerium conversion layer of the multilayer coatings. (a) Ce(IV)/(PEI/PAA)5. (b) Ce(IV)/(PEI/PAA)10. (c) Ce(IV)/(PEI/PAA)15. (d) Ce(IV)/(PEI/PAA)20. .................................................................................. 82

Figure 6.7 The limited self-healing behavior of the sample of Ce(IV)/(PEI/PAA)5. (a) Before immersion in water for 10 min. (b) After immersion in water for 10 min. ......................... 83

Figure 6.8 The self-healing behavior of the multilayer coatings. (a) The cut with a 10-microns cut on the sample of Ce(IV)/(PEI/PAA)10. (b) The sample of Ce(IV)/(PEI/PAA)10 after immersion in water for 10 min. (c) The cut with an 11-microns cut on the sample of Ce(IV)/(PEI/PAA)10. (d) The sample of Ce(IV)/(PEI/PAA)10 after immersion in water for 20 min. (e) The cut with a 20-microns cut on the sample of Ce(IV)/(PEI/PAA)20. (f) The sample of Ce(IV)/(PEI/PAA)20 after immersion in water for 10 min. (g) The cut with a 22-microns cut on the sample of Ce(IV)/(PEI/PAA)20. (h) The sample of Ce(IV)/(PEI/PAA)20 after immersion in water for 20 min. .................................................................................. 84

Figure 6.9 The swelling behavior of the multilayer coatings. (a) The water uptake. (b) The swelling ratio. .......................................................................................... 87

Figure 6.10 The Vickers hardness of the multilayer coatings .................................................................................. 88

Figure 7.1 The preparation scheme of the GO incorporated multilayer coating ......................... 92

Figure 7.2 The SEM images of the (a) graphene oxide and (b) the surface of Ce(IV)/PEI/GO/(PEI/PAA)10 ........................................................................................................ 93

Figure 7.3 The XRD patterns and Raman spectra of the multilayer coating with and without GO. (a) XRD pattern. (b) Raman spectra. ................................................................. 94

Figure 7.4 The TGA and DSC results of the sample of (a) Ce(IV)/(PEI/PAA)10 and (b) Ce(IV)/PEI/GO/(PEI/PAA)10. ........................................................................ 96

Figure 7.5 The self-healing behavior of the sample of Ce(IV)/PEI/GO/(PEI/PAA)10. ............ 97

Figure 7.6 Comparison of the Vickers hardness for the samples of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 before and after immersion. ........................................ 98
Figure 7.7 The EIS results of Bode phases at (a) 0.5 h, (b) 2 h, (c) 4 h, (d) 24 h, (e) 48 h and (f) 72 h.

Figure 7.8 The EIS results of Bode impedances at (a) 0.5 h, (b) 2 h, (c) 4 h, (d) 24 h, (e) 48 h and (f) 72 h.

Figure 7.9 The EIS results of Nyquist plots at (a) 0.5 h, (b) 2 h, (c) 4 h, (d) 24 h, (e) 48 h and (f) 72 h.

Figure 7.10 The equivalent circuits of the EIS results.

Figure 7.11 The polarization resistance and protection efficiency as a function of time. (a) The polarization resistance. (b) The protection efficiency.

Figure 7.12 The surface morphology and chemical distribution of the sample of Ce(IV)/(PEI/PAA)10.

Figure 7.13 The surface morphology and chemical distribution of the sample of Ce(IV)/PEI/GO/(PEI/PAA)10.

Figure 7.14 The corrosion products analysis of the sample of Ce(IV)/(PEI/PAA)10 after 72 hours EIS tests. (a) The XRD pattern. (b) The Raman spectra.

Figure 7.15 The corrosion products analysis of the sample of Ce(IV)/PEI/GO/(PEI/PAA)10 after 72 hours EIS tests. (a) The XRD pattern. (b) The Raman spectra.

Figure 7.16 The protection mechanism of the sample of Ce(IV)/(PEI/PAA)10.

Figure 8.1 SEM images of (a) bare EGS and (b) (PEI/PAA)20.

Figure 8.2 The XRD patterns and Raman spectra of bare EGS and (PEI/PAA)20. (a) The XRD patterns. (b) The Raman spectra.

Figure 8.3 The self-healing behavior of the samples of (PEI/PAA)20. (a) A single cut on the surface of (PEI/PAA)20. (b) The surface immersed in water after 10 min. (c) Multiple cuts on the surface of (PEI/PAA)20. (d) The surface immersed in water after 10 min.

Figure 8.4 The Bode phases of the EIS results at (a) 0.5 h, (b) 2 h, (c) 4 h, (d) 24 h, (e) 48 h and (f) 72 h.

Figure 8.5 The Bode impedance of the EIS results at (a) 0.5 h, (b) 2 h, (c) 4 h, (d) 24 h, (e) 48 h and (f) 72 h.

Figure 8.6 The Nyquist plots of the EIS results at (a) 0.5 h, (b) 2 h, (c) 4 h, (d) 24 h, (e) 48 h and (f) 72 h.
Figure 8.7 The equivalent circuits for the EIS results. (a) Model 1. (b) Model 2. (c) Model 3. 130
Figure 8.8 The polarization resistance of bare EGS and (PEI/PAA)20. ................................. 131
Figure 8.9 The SEM and EDS images of lightly and heavily corroded spots on bare EGS. (a) Lightly corroded spot. (b) Heavily corroded spot. ................................................................. 133
Figure 8.10 The SEM and EDS images of lightly and heavily corroded spots on (PEI/PAA)20. (a) Lightly corroded spot. (b) Heavily corroded spot. ................................................................. 134
Figure 8.11 The XRD patterns and Raman spectra of lightly corroded and heavily corroded spots on the sample of bare EGS. (a) XRD patterns. (b) Raman spectra. ................................. 136
Figure 8.12 The XRD patterns and Raman spectra of lightly corroded and heavily corroded spots on the sample of (PEI/PAA)20. (a) XRD patterns. (b) Raman spectra. ........................................ 139
Figure 8.13 The degrading process of bare EGS. (a) The intact bare EGS. (b) The zinc layer started to dissolve. (c) The corrosion product of sodium carbonate started to grow. (d) The crack initiated on the zinc layer. ........................................................................................................ 141
Figure 8.14 The degrading process of (PEI/PAA)20. (a) The intact (PEI/PAA)20. (b) The PEI/PAA multilayers started to dissolve. (c) The crack initiated on the PEI/PAA multilayers. (d) The crack grew and the corrosion products formed on the surface. ............................................. 142
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPE</td>
<td>Constant Phase Element</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EGS</td>
<td>Electrogalvanized Steel</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene Oxide</td>
</tr>
<tr>
<td>IEP</td>
<td>Isoelectric Point</td>
</tr>
<tr>
<td>MMT</td>
<td>Montmorillonite</td>
</tr>
<tr>
<td>PAA</td>
<td>Poly(acrylic acid)</td>
</tr>
<tr>
<td>PEI</td>
<td>Poly(ethylene imine)</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1. Background of self-healing

Artificial materials suffer from unexpected damages and continuous degradation during all their service life. Scientists and engineers are trying to find a way to extend the service life of artificial materials. Increasing the toughness, mechanical strength and hardness of the materials could be a solution to the problem. For example, the seashell nacre evolved to have a superior toughness to protect itself. Based on this concept, scientists prepared an artificial nacre with the polyelectrolyte of poly(diallyldimethylammonium chloride) (PDADMAC) and the natural clay of montmorillonite (MMT) [1]. However, the low flexibility of this material limited its practical application. Biological systems provided another idea to design the materials with an extended service life, for example, human skins. The response of human skin to wounds is initiated by the blood clotting [2]. After that, more biological materials are delivered to the damaged area to heal the wound by skin regeneration [3]. This recovery process is regarded as self-healing and was set to be the benchmark of engineered self-healing materials [4]. However, it is a great challenge to fabricate a self-healing material with all the properties of human skins due to its nature of sophistication. S.R. White, the pioneer researcher on self-healing materials, defined self-healing as “the ability to repair damage and restore lost and degraded properties or performance using resources inherently available to the system” [2]. With the development of self-healing materials, multiple biomimetic designs have been proposed and applied including the intrinsic and the extrinsic self-
healing materials [5]. The extrinsic self-healing materials rely on the release of healing agents which are embedded in the matrix; while the intrinsic self-healing materials rely on the re-association of non-covalent bonding. However, the main drawback of the extrinsic self-healing materials is that they cannot heal multiple damages at the same position due to the depletion of the healing agents. Therefore, the focus of the study on self-healing materials is the intrinsic self-healing materials. Nonetheless, the low mechanical strength and unstable status of the existed intrinsic self-healing materials have limited their practical applications.

1.2. Motivations

1.2.1. The self-healing acrylic elastomer VHB 4910

Recently, it was discovered that a commercially available elastomer, VHB 4910 manufactured by 3M company, demonstrated a good compromise of the mechanical strength and the self-healing ability [6]. This material can be stretched to 10 times of its original length with a toughness reaching up to ~1.91 MJ/m$^3$. The toughness almost doubled the value (~1MJ/m$^3$) of the self-healing copolymer of acrylamide and acrylate [7]. Due to its excellent mechanical strength and electro-active properties, this material showed a potential to be used as a dielectric actuator [8–13]. In addition, its application in artificial muscles has been suggested [14,15]. However, few studies have been conducted on the origin of its viscoelasticity and self-healing properties [6]. Steinmann et al. [16] has studied its viscoelasticity using mathematical models but did not explain the origin of its viscoelasticity. The solid state of VHB 4910 is an autonomous self-healing material which retains the same property in the ambient environment [6]. Unlike other self-healing materials that require energy input such as hot water treatment [17], UV light [18], or gel type materials that deteriorate with the evaporation of solvents [19,20], VHB 4910 can heal in the ambient environment without human intervention. This material is clarified to be an acrylic material. However, the detailed chemical structure of this material is not disclosed. Because of the acrylic materials usually have the carbonyl bonds as their substantial structure, it was hypothesized that the hydrogen bonding which was formed by the carbonyl bonds could be the reason for the self-healing property. In addition, the self-healing ability increased with the healing time and temperature. Therefore, the molecular chain diffusion process could also contribute to the self-
healing property and this assumption could be confirmed with the results of tensile tests. Therefore, it is important to understand the chemical structure and the self-healing mechanism of this acrylic elastomer. These results could stimulate the design and fabrication of self-healing materials.

1.2.2. The importance to protect magnesium alloys

Preparing a self-healing coating is one of the most promising applications of self-healing materials. Magnesium alloy AZ31 has been applied to various industrial applications including the automotive industry, electronics, aerospace and biomedical applications because it has a high strength to weight ratio, high damping capacity and degradable property which are important for biomedical applications [21–26]. The production of magnesium alloy has doubled during the last 15 years due to the demand for weight reduction in the automotive and electronics industry [27]. However, the soft surface and the low corrosion resistance of magnesium alloy have limited its service life. Because of the soft surface of the magnesium alloys, it is easy to scratch the surface. By preparing a self-healing coating on the surface, the service life of the products made by magnesium alloys could be extended. Corrosion is another great challenge faced by human society. It was estimated that the corrosion damage cost around €200 billion in Europe and $300 billion in the United States [28]. Therefore, preparing a self-healing coating with an improved corrosion resistance became necessary for the further applications of magnesium alloys.

1.2.3. Addition of graphene oxide

Natural clays may be added to a polymer matrix to improve the mechanical strength and temperature response [29,30]. Furthermore, it was found that clay could be added in the nanocomposite hydrogel to introduce the self-healing ability [31]. This self-healing property was attributed to the re-association of hydrogen bonding formed between the clay sheets and the polymer. Similar to clay, graphene oxide (GO) can also be added to a polymer matrix to improve the mechanical strength and thermal response of the resulting composite [32]. GO is a modified product of graphene by introducing oxygen-containing functional groups to the graphene lattice [33]. It was found that the GO-added polymer composites demonstrated improved thermal stability compared to clay-based polymer composites [34]. The functional groups of GO are critical for the
properties of GO/polymer composites because they can interact with the polymer matrix by forming non-covalent bonding including hydrogen bonding. It was found that the GO-based polymer composites may demonstrate a self-healing ability due to hydrogen bonding networks [35]. Therefore, GO could be expected to improve the self-healing ability of coatings by the formation of hydrogen bonding in the coating. In addition, the GO/polymer composites have also been developed to form air separation membranes due to their superior barrier property [36]. Such membranes were found to significantly decrease the oxygen permeability. Thus, it was expected that by adding GO into the polymeric coating on magnesium alloy, the corrosion resistance could be further improved due to enhanced barrier property.

1.3. Objectives

Lack of mechanical strength has limited the practical applications of self-healing materials. However, VHB 4910 exhibited a good compromise between the mechanical strength and the self-healing ability. This balanced behavior motivated us to understand the self-healing mechanism of VHB 4910. In addition, applying the similar materials to coat the magnesium substrate could offer an efficient protection to the substrate. By adding graphene oxide, such coatings were also expected to enhance the self-healing ability and corrosion resistance.

Considering the discussion above, the objectives of this research could be simply listed as:

1. To determine the self-healing ability and understand the self-healing mechanism of the acrylic elastomer.

2. To develop a self-healing and anticorrosion coating on the magnesium and galvanized steel substrate.

3. To define the effect of GO on the self-healing and anticorrosion properties of the coating.

The thesis is systematized using the following chapters.

Chapter 2. In this chapter, a review of the mechanism of different self-healing materials including the intrinsic and extrinsic self-healing materials was presented. The application of the self-healing
materials on the anticorrosion coating, superhydrophobic coating, and barrier membranes were also discussed.

Chapter 3. The working mechanisms of the main techniques used to prepare and characterize the materials including tensile tests, layer-by-layer (LbL) assembly, electrochemical impedance spectroscopy (EIS), X-ray diffraction (XRD) and Raman spectroscopy were discussed.

Chapter 4. The mechanical and viscoelastic properties of the acrylic elastomer were characterized and the self-recovery behavior in the cyclic tensile tests was explained. This chapter is fundamental to describe the self-healing ability of this material. The results of this chapter have been published in “F. Fan, J. Szpunar, Characterization of viscoelasticity and self-healing ability of VHB 4910. Macromolecular Materials and Engineering, 300 (2015), 99 – 106”.

Chapter 5. The self-healing efficiencies of the acrylic elastomer under room temperature and elevated temperature for different healing times were tested. The self-healing mechanism was discussed by the results of the tensile tests and the Raman spectra. Object 1 was completed and reported in Chapter 4 and 5. The results of this chapter have been published in “F. Fan, J. Szpunar, The self-healing mechanism of an industrial acrylic elastomer. Journal of Applied Polymer Science, 132 (2015), 42135”.

Chapter 6. The self-healing anticorrosion coating was prepared on the magnesium alloy and the self-healing ability and corrosion resistance of this coating was tested. The self-healing ability was explained by swelling tests. This chapter partially reached objective 2 of preparing the polymer coating on magnesium alloy. Part of the results of this chapter has been published in “F. Fan, C.Y. Zhou, X. Wang, J. Szpunar, Layer-by-Layer assembly of a self-healing anticorrosion coating on magnesium alloys. ACS Applied Materials & Interfaces, 7 (2015), 27271 – 27278”.

Chapter 7. GO was added to the self-healing anticorrosion coating and the role of GO in the coating was explained. The self-healing ability of the coating with GO was confirmed. The excellent corrosion resistance of GO was also analyzed using SEM, EDS, and Raman spectroscopy. This chapter finished objective 3. Part of the results of this chapter have been published in “F. Fan, C.Y. Zhou, X. Wang, J. Szpunar, Layer-by-Layer assembly of a self-healing anticorrosion coating on magnesium alloys. ACS Applied Materials & Interfaces, 7 (2015), 27271 – 27278”.
Chapter 8. The self-healing anticorrosion coating was applied on the galvanized steel and the self-healing ability of this coating on galvanized steel was confirmed and the degradation mechanism of this coating on electrogalvanized steel was analyzed. This chapter proved the versatility of this multilayer coating and finished objective 2 of preparing the polymer coating on electrogalvanized steel.

The Copyright and permission for reusing the context, figures, and tables of these published results have been attached at the end of the thesis.
CHAPTER 2

LITERATURE REVIEW

2.1. Overview

During last decades, many different kinds of self-healing materials have been developed [2,37]. Wool [38] has theoretically calculated the influence of molecular weight and self-healing time on the behavior of self-healing materials. Urban et al. [4] reviewed the self-healing process using the thermodynamic model.

In this chapter, the mechanism of self-healing materials was discussed. The self-healing materials could generally be divided into two categories: intrinsic self-healing materials and extrinsic self-healing materials [5]. The intrinsic self-healing materials are dependent on non-covalent bonding of the materials, for example, the type of hydrogen bonding, hydrophobic interactions, and electrostatic attractions. On the contrary, the extrinsic self-healing materials are dependent on healing agents which are embedded in the material matrix. The applications of self-healing materials were also discussed in this chapter. The self-healing materials have been applied to various laboratory type applications including novel biological materials [20,39], protective coatings [40,41], electronic skin [42], drug delivery [43] and batteries [44]. The studies focused on the applications of self-healing anticorrosion coating, self-healing superhydrophobic coating and self-healing barrier membranes.
2.2. The mechanism of self-healing materials

2.2.1. Hydrogen bonding

Hydrogen bonding is one of the reversible non-covalent bonding which forms between the hydrogen atom and another atom. In 2008, Leibler et al. [45] prepared the hydrogen bonding assisted self-healing rubber via the synthesis of fatty acid and urea. The fatty acid was made from the vegetable oil and composed of carboxylic acid functional groups (COOH). The urea consisted of the amine group (N-H). The C=O groups of COOH played a role as the hydrogen bonding acceptors while the N-H groups were the hydrogen bond donor. When the two groups were mixed together, they formed strong hydrogen bonding in the materials. The samples were cut in the middle and brought together for certain healing times. The healed samples sustained an elongation of 2 mm/mm at room temperature. This self-healing behavior was attributed to the re-association of hydrogen bonding at the cutting interfaces. In addition, the self-healing ability was found to increase with time. The healing process started after immediate joining the two separated parts. When there was a time delay before the contact was made, the self-healing ability was found to decrease. This was most likely due to the creation of pairs between the free hydrogen bond acceptors and donors within each part of the cut specimen. Thus, lower number of active hydrogen bonds acceptors and donors were available for self-healing. The in situ FT-IR results showed that when the temperature increased, wavenumber of the C=O stretching shifted to a higher frequency while the wavenumber of the N-H bending shifted to a lower frequency [46]. This oppositely shifting behavior confirmed the existence of hydrogen bonding as high temperatures were believed to break the hydrogen bonding [47]. The hydrogen bonding can help generate another kind of non-covalent bonding which is called π - π stacking [48]. π - π stacking is the interaction between the folded aromatic molecular chains which are rich in π-electrons [49]. Colquhoun et al. [49] prepared a π - π stacking self-healing material using the complexation of a polyimide with a pyrenyl end-capped polyamide. This material can heal a cut with a width of 75 μm upon heating up to 90 degrees Celsius.

Because of the property of hydrogen bonding, the pH value was also found to influence the self-healing ability [32]. Varghese et al. [39] prepared a rapid self-healing material using acryloyl-6-aminocaproic acid (A6ACA). The hydrogen bonding of A6ACA was formed by the COOH groups which acted as both acceptors and donors. The A6ACA lost the self-healing ability when the pH
value was greater than the ionization point of COOH groups, because the COOH was deprotonated to be COO⁻ and lost the function of being the hydrogen bonding donors. However, the COO⁻ can be protonated in an acid environment when the pH value is less than the ionization point of COOH groups and thus the self-healing ability of the materials can be restored. Therefore, the pH value and the ionization point of the functional groups are important for the self-healing property [35].

It was found that by adding clay or graphene oxide into the polymer matrix, the mechanical strength of the polymer was improved [31,50]. When the clay or graphene oxide was uniformly dispersed in the polymer matrix, they formed hydrogen bonding with the polymer molecules and acted as the cross-links. The mechanical strength increased because of the growth of cross-link density [30,32]. Clay was first added to the poly(N-isopropylacrylamide) as the reversible crosslinkers [51]. It was found that the concentration of clay strongly influenced the mechanical strength and the swelling/de-swelling behaviors of the polymer [29]. Haraguchi et al. [31] further confirmed that the polymer/clay network demonstrated a self-healing ability due to the hydrogen bonding formed between the clay and the polymer. However, when the polymer was fully synthesized its mechanical strength was poor as the hydrogen bonding is weaker than the covalent bonding [52,53]. Therefore, introducing the covalent cross-links to the polymer matrix could improve the mechanical strength of the materials [54]. Guan et al. [55] prepared a hydrogen bonding polymer via the synthesis of acrylate amide with polystyrene. The acrylate amide formed hydrogen bonding between the N-H groups and the C=O groups to provide the self-healing ability to this material. The polystyrene played a role as covalent crosslinks and improved the mechanical strength. The original sample of this material was stretched to a strain around 9 mm/mm with a fracture stress of 0.56 MPa and the healed sample recovered to a strain greater than 700% after 24 h with a fracture stress of 0.35 MPa. This material demonstrated a good balance between the self-healing ability and the mechanical strength.

2.2.2. Hydrophobic interactions

Hydrophobic interactions describe the entanglement of the aliphatic molecular chains. It was found that a double network polymer consisting of a weak and a strong network was much tougher than the single network polymer [56]. This improvement was due to that the soft network acted as a sacrificial network which dissipated much energy during the elongation test [57]. Gong et al. [58]
prepared a lamellar structure hydrogel with a soft network consisting of hydrophobic interactions. The cyclic tensile tests were applied to the hydrogels and the results showed a significant hysteresis behavior. The hysteresis behavior was observed because of the energy dissipation accompanied with the dissociation of the hydrophobic interactions. Furthermore, the hysteresis was almost recovered with the increase of recovery time to 15 min. This self-recovery property was attributed to the re-association of the hydrophobic interactions after the loading force was released. In addition, the energy dissipation was found to be independent on deformation when the strain was less than 100% but strongly dependent on deformation when the strain was greater than 100% [59].

The above results confirmed the reversibility of the hydrophobic interactions which could be employed to develop a self-healing material. Tuncaboylu et al. [60] prepared a self-healing hydrogel via the polymerization reaction of a large hydrophobic stearyl methacrylate with a hydrophilic acrylamide in the presence of a surfactant of sodium dodecyl sulfate (SDS). This hydrogel exhibited a self-healing ability at room temperature. The healed samples were stretched to a strain about 3.6 mm/mm which is similar to the original samples. It was found that the surfactant of SDS played an significant role in the self-healing behavior of this polymer. The polymer synthesized in the presence of SDS demonstrated a complete 100% self-healing, while no self-healing behavior was observed in the polymer without SDS [61]. This was probably due to the fact that SDS increased the solubility of the hydrophobic interactions which generated the reversible cross-links [62]. However, in the absence of SDS, the hydrophobic molecular chains collapsed and formed a heterogeneous structure with the permanent cross-links which cannot be restored after damage. This hypothesis was confirmed by a higher breaking stress and a lower breaking strain of the polymer without SDS. However, a self-healing polymer was fabricated by the synthesis of acrylamide and dimethyldodecyl(2-acrylamidoethyl)ammonium bromide in the absence of surfactants [63]. This polymer exhibited a self-healing efficiency of 74% after 7 days.

In addition to the surfactant, the length of the alkyl chains is critical to the mechanical strength and self-healing ability of the polymer. It was found that the alkyl side chains with 18 carbon atoms demonstrated the best self-healing ability [7]. This was due to that this structure reached a good balance between the flexibility of the molecular chains and the available hydrophobic interactions. Based on this study, the covalent crosslinker of $N,N'$-methylenebis(acrylamide) was introduced to the methacrylate with 18 carbon atoms on the side chains [64]. It was found that the mechanical
strength of this polymer was 24 times higher than that of the polymer without the covalent crosslinker. Furthermore, this polymer also had a self-healing efficiency of 80% due to the existence of the reversible hydrophobic interactions.

The hydrophobic interactions can also work with the hydrogen bonding to enforce each other [65]. The polymer synthesized by the stearyl methacrylate with the poly(acrylic acid) demonstrated an extreme elongation up to 5 mm/mm [66]. Compared to the sample synthesized with polyacrylamide which cannot form hydrogen bonding, this polymer demonstrated a strong self-healing ability with at least 80% healing efficiency at an elevated temperature of 80 degrees Celsius after 30 min. This property was due to the synergy between the hydrogen bonding and the hydrophobic interactions [39].

2.2.3. Electrostatic attractions

Electrostatic attractions are represented by the Coulomb force between the oppositely charged molecules. Creton et al. [67] found that the polymer fabricated by the modified poly(acrylic acid) exhibited a hysteresis behavior at a high strain deformation. The pH value of poly(acrylic acid) was tuned to 7 by sodium hydroxide. This pH value was greater than the ionization point of acrylic acid. Therefore, the negatively charged polyelectrolytes were formed and induced the hysteresis behavior. Because of the reversibility of the electrostatic attractions, the polymers with opposite charges can be applied to prepare the self-healing materials. In 2013, Gong et al. [17] developed a self-healing polymer via the assembly of the negatively charged polyanion with the negatively charged polycation. They found that this polymer recovered 100% of the hysteresis loop after 120 min and healed 30% of the mechanical strength after 1 h. This self-recovery and self-healing ability was attributed to the reversibility of the electrostatic attractions formed by polyelectrolytes. In addition to the polymer synthesized by the polymerization reaction, layer-by-layer (LbL) technique provides another simple tool to prepare the polymer by the electrostatic attractions [68]. Sun et al. [69] made a polymer via the LbL assembly of poly(acrylic acid) (PAA) with poly(ethylene imine) (PEI) on glass slides. The pH value of PAA was tuned to 3 with sodium hydroxide to produce the negatively charged polyelectrolytes while the pH value of PEI was tuned to 10.5 with hydrochloride acid to form the positively charged polyelectrolytes. This polymer
healed the cut with a width of 50 microns in 5 min in the presence of water. The polymer swelled in the presence of water and then the electrostatic attractions bonded the cutting interfaces together.

Not only the charged macromolecules but also the charged metal ions produce the self-healing polymer. Metal ions were used to form the ionic bond with the negatively charged polymers via the electrostatic attractions and the product was defined as the metal complexation [70]. Del Campo et al. [71] fabricated a self-healing gel via the metal complexation of Fe$^{3+}$ and catechol. The separated two parts of this gel healed in 3 min. In addition, the physical property of this Fe$^{3+}$-catechol can be tuned by pH value because the cross-links of electrostatic attractions are strongly affected by the pH value [72]. Zn$^{2+}$ can also be used to prepare the self-healing polymers. Weder et al. [18] made a metal complexation by Zn$^{2+}$ which had a 100% self-healing ability after the exposure to ultraviolet light. This was because that the energy of light was converted to heat which induced the dissociation of the electrostatic attractions and therefore allowed for a high mobility of the molecular chains. As a result, the molecular chains diffused through the interface at the cut and healed the cut. When the ultraviolet light was turned off, the electrostatic attractions reformed.

Guan et al. [73] fabricated a metal-complexation polymer by Zn$^{2+}$ and imidazole. This polymer demonstrated a self-healing behavior in the ambient environment without any external stimuli. In addition, calcium ions were also used to synthesize the self-healing polymer [74].

2.2.4. **Reversible covalent bonding**

The covalent bonding is formed by sharing electrons within atoms and therefore is usually regarded as non-reversible bond. However, it was found that some materials underwent ring-opening reaction under elevated temperatures and formed new covalent bonding with the available reactive functional groups [75]. This concept of reversible covalent bonding can be applied to fabricate the self-healing materials. The reversible Diels-Alder (DA) reaction was comprehensively studied [76]. In 2002, Chen et al. [77] prepared an organic material which showed self-healing ability via the reversible DA reaction. This material exhibited a self-healing efficiency of 57% after heated at 150 degrees Celsius in the nitrogen environment for 2 h. They found that about 30% cross-links disconnected at a temperature above 120 degrees Celsius and re-associated upon cooling. It was the open and close reaction of the covalent bonding that provided the self-healing ability to this polymer. In addition, the multiple heating steps can further improve
the self-healing efficiency. Sodano et al. [78] synthesized the polyurethanes by the DA reaction between furan and maleimide and healed the cracks of this material under 135, 90 and 70 degrees Celsius for 2 h. A self-healing efficiency of 80% was obtained after the multiple heating steps which ensured a uniform cooling and retro-DA reaction in the samples. In addition to heating, the ultraviolet (UV) light can also trigger the reversibility of the covalent bonding [79,80]. Urban et al. [81] prepared an oxetane-substituted chitosan polyurethane which healed in 1 h upon the exposure to the UV light. It was the chitosan chain scission reaction that formed crosslinks with the reactive ends which were made by the mechanical damage.

Without the external stimuli, the polymers produced by the reversible DA reaction were also found to demonstrate a self-healing ability. Yoshie et al. [82] prepared the polymer by the DA reaction between the bio-based furan and maleimide. They discovered that by changing the ratio of furan to maleimide, the synthesized polymer obtained a self-healing efficiency of 75% in 5 days and the chloroform solvent further improved the self-healing efficiency to 90%. However, this 5 days’ healing time was still too long for practical applications. Matyjaszewski et al. [83] developed another self-healing polymer with the disulfide bonds. This polymer healed a 30 microns wide cut in 1 h in the ambient environment. This excellent self-healing ability was attributed to the regeneration of the disulfide bond [84].

2.2.5. Encapsulated healing agent

The extrinsic self-healing employs the embedded self-healing agents to heal the damage. During the earliest efforts, inorganic materials were used to make self-healing agents. Sugama et al. [85] sealed the cut damage by the expansion of monocalcium aluminate (CaO·Al₂O₃) and calcium bialuminate (CaO·2Al₂O₃). However, this process was only observed at 200 degrees Celsius in the presence of carbon dioxide for 24 hours. After that, the central focus of developing healing agent is on the organic polymeric materials because the polymerization reaction of these materials can happen at room temperature. In 2001, White et al. [86] prepared an autonomous self-healing polymer based on the ring-opening metathesis polymerization of dicyclopentadiene (DCPD) at room temperature. The healing agent of DCPD was encapsulated in the urea-formaldehyde microcapsules to separate from the matrix. When the crack happened, the microcapsules were ruptured and released the healing agent to the crack. The polymerization occurred in the presence
of Grubbs’ catalyst at room temperature to heal the crack. The embedded microcapsules also increased the toughness and fatigue life of the matrix material [87,88].

Kirkby et al. [89] embedded the shape memory alloy with the healing agent in the polymer matrix. They found that this system had a better self-healing efficiency because the shape memory alloy decreased the crack volume. These kinds of self-healing materials have been reported with different healing efficiencies ranging from 45% to 90% [90,91]. Such unstable behavior was mainly due to the non-uniform dispersion of the catalyst [92]. It was found that the smaller catalyst particle could be dissolved more uniformly and thus induced a better healing ability [93]. However, the small catalyst particle was also attacked by the curing agent of the matrix which led to a poor healing efficiency. To solve this paradox, Moore et al. [92] encapsulated the catalyst by paraffin wax. This method separated the influence of the curing agent from that of the catalyst. Based on this design concept, Sottos et al. [94] embedded the encapsulated healing agent and catalyst in the poly(dimethyl siloxane) elastomer and obtained a healing efficiency between 70% - 100%.

The significant drawback of the microcapsule-based self-healing materials is that they can heal the crack only once on a given spot because of the depletion of the healing agent. To solve this problem, a three-dimensional vascular network was developed to deliver the healing agent to the crack position [95]. The liquid healing agent was filled in the vascular networks while the catalyst was applied to the top surface. This system provided a repeated healing ability to the damages. However, the existence of catalyst is still a potential problem with the system. Yang et al. [96] developed another healing agent of diisocyanate for the polymerization. This healing agent reacted in the absence of catalyst which significantly improved the stability of the microcapsule-based self-healing system.

2.3. The application of self-healing materials

2.3.1. Self-healing anticorrosion coating

The self-healing anticorrosion coating is one of the most promising applications of self-healing materials. Self-healing anticorrosion coatings have attracted attention from the researchers as their potential to recover from the attack of the corrosive medium. In the beginning, the study focused on the recovery of corrosion resistance because the primary objective of the coating is to prevent
the substrate from corrosion. Chromium conversion layer was widely used because of its excellent corrosion resistance [97]. However, the carcinogenic problem of hexavalent chromium ions has resulted in the prohibition of the use of chromium coating in Europe in 2007 [98]. Therefore, looking for a replacement of Chrome has become the critical issue. The earth clay element, cerium, has been studied to be the candidate during recent years because it has similar anticorrosion property but is environment-friendly [99]. Montemor et al. [23] prepared the cerium oxide layer on the magnesium alloy by simply dipping the magnesium alloy into the cerium nitrate solution. The cerium-based conversion layer was found to suppress both the anodic and cathodic corrosive reactions. This behavior was attributed to the formation of cerium hydroxide by the cerium ions and the hydroxyl ions which were produced by the corrosion reactions. The cerium-based conversion layer was adopted in many other studies and applied to the development of anticorrosion coatings [100–102].

Sol-gel is often used to prepare the anticorrosion coating. It was found that the zirconia nanoparticles embedded in the sol-gel matrix improved the corrosion resistance because the nanoparticles blocked the defects in the coating [103]. Zheludkevich et al. [104] prepared a sol-gel coating containing the zirconia nanoparticles with cerium nitrate. The cerium ions were loaded in the zirconia nanoparticles as the corrosion inhibitors. The authors found that the cerium-loaded coating further improved the corrosion resistance because the extended release of cerium ions suppressed the corrosive reaction on the substrate [105]. The smaller size of the nanoparticles was more efficient in improving the corrosion resistance [106]. In addition to the cerium ions, multiple organic materials have been adopted as an effective corrosion inhibitor [107]. Ferreira et al. [108,109] used titania nanoparticles as a reservoir for the organic corrosion inhibitors in the sol-gel coating. This hybrid coating exhibited an enhanced corrosion resistance. However even if the corrosion inhibitors were loaded on the nanoparticles, the release of the inhibitors was still out of control. Polyelectrolytes were applied to fabricate the shell of nanoparticles via LbL assembly and allowed to control the release of corrosion inhibitors [110,111]. It was found that the weak polyelectrolyte pairs of poly(allylamine hydrochloride)/poly(methacrylic acid) (PAH/PMAA) provided an immediate release of the corrosion inhibitor while the shells containing at least one strong polyelectrolyte including the pairs of poly(diallyldimethylammonium chloride)/poly(styrene sulfonate) (PDADMAC/PSS) and poly(allylamine...
hydrochloride)/poly(styrene sulfonate) (PAH/PSS) offered a gradual release of the corrosion inhibitor [112].

LbL can also be applied to fabricate the anticorrosion coating on metals. Andreeva et al. [41] prepared a self-healing anticorrosion coating by assembling poly(ethylene imine) and poly(styrene sulfonate) on the aluminum alloy via layer-by-layer (LbL) method. This multilayer coating showed an improved corrosion protection to the aluminum alloy which was probably due to the buffering effect of the polyelectrolyte multilayers [113]. Different combinations of polyelectrolytes including weak-weak (PEI/PAA), weak-strong (PEI/PSS) and strong-strong (PDADMAC/PSS) were studied for the corrosion resistance [114]. The pair of weak-strong polyelectrolytes demonstrated the best corrosion resistance while the pair of weak-weak exhibited a self-healing behavior which suppressed the corrosion reaction. Furthermore, the multilayer polyelectrolytes coating worked together with the sol-gel coating to provide a better corrosion resistance [115]. However, as reviewed by Andreeva et al. [116], most of the self-healing anticorrosion coating can only recover the corrosion resistance ability instead of healing the damage.

2.3.2. Self-healing superhydrophobic coating

The superhydrophobic coating has wide applications ranging from self-cleaning to antiadhesive coating. Superhydrophobicity is observed when the surface exhibits a water contact angle larger than 150° [117]. To achieve the superhydrophobicity, the surface is required to demonstrate a low surface energy [118]. Therefore, fluoro-modified materials, which have a low surface energy, are usually applied to prepare the superhydrophobic coating [119]. Sun et al. [120] prepared a self-healing superhydrophobic coating using the chemical vapor deposition of 1H,1H,2H,2H-perfluorooctyltriethoxysilane (POTS) on the LbL assembled poly(allylamine hydrochloride)+sulfonated poly(ether ether ketone)/poly(acrylic acid) (PAH+SEEK/PAA) multilayers. This coating exhibited a water contact angle of 157° with a sliding angle less than 2°. In addition, this coating recovered the superhydrophobicity from scratches for multiple times in the environment with a room humidity of 40% for 4 h. This recovery property was attributed to the self-healing ability of the underlying LbL multilayers which swelled and brought the preserved POTS to the surface. Furthermore, it was found that the silica and titania nanoparticles induced a superhydrophobicity to the coating [121–123]. Wu et al. [124] prepared a self-healing
superhydrophobic coating by mixing the fluoro-modified silane with silica and titania nanoparticles. Because of the photosensitivity of the titania nanoparticles, this coating recovered a water contact angle of 150° after UV irradiation which was closer to the water contact angle of 155° of the original samples. The self-healing of the superhydrophobic coating can also be achieved by the healing agent encapsulated in the hydrophobic microcapsules. Yang et al. [125] prepared a self-healing superhydrophobic coating by embedding the poly(urea-formaldehyde) microcapsules in the coating matrix. These microcapsules induced the coating with a water contact angle of 160°. In addition, the encapsulated healing agent of hexamethylene diisocyanate (HDI) can be released to heal the crack. If a coating can repel both water and oil, it is regarded as an omniphobic or amphiphobic coating which is more difficult to achieve due to the low surface energy of organic oil [126]. Wong et al. [127] prepared an omniphobic coating by adding a fluorinated lubricating liquid onto the nanostructured surface. This lubricating liquid and the nanostructured surface is the key for the omniphobicity. Furthermore, when damage happened, the capillary force drove the lubricating liquid to the scratches and restored the omniphobicity.

### 2.3.3. Self-healing barrier membranes

The barrier membranes have acquired considerable research attention because of its selectivity of ions and property of gas separation [128]. The selectivity of ions is ascribed as the ability to separate the mono and divalent ions or the charged ions and neutral molecules. Bruening et al. [129] prepared a multilayer consisting of poly(allylamine hydrochloride)/poly(styrene sulfonate) (PAH/PSS) on a porous alumina. This membrane demonstrated a high anion selectivity of Cl⁻/SO₄²⁻ and Cl⁻/Fe(CN)₆³⁻. This separation effect was attributed to the Donnan exclusion of the divalent ions [130]. It was found that the polyelectrolyte membrane also had a high selectivity of the mono and divalent cation such as Na⁺/Mg²⁺ and K⁺/Mg²⁺ [130,131]. The permeability of all these ions was strongly dependent on the cross-link density of the polyelectrolytes. The study shows that the prepared polyelectrolyte membranes with a higher charge density demonstrated a lower swelling ability and a slower solute transport [132]. In addition to the selectivity of charged ions, the separation of charged ions and neutral molecules is relevant to practical applications as well. In 2014, Phillip et al. [133] fabricated a mixed mosaic membranes made of the lined up nanotubes and a porous support. The nanotubes were prepared by LbL assembly of poly(acrylic
acid)/poly(allylamine hydrochloride) (PAA/PAH) on a sacrificial template and terminated by the positively charged PEI and negatively charged PSS. This mosaic membrane demonstrated a high ionic flux with the ability to enrich the sodium chloride concentration.

In addition to the ion separation, the polyelectrolyte membranes can be applied to separate gasses. McCarthy et al. [134] found that the PAH/PSS multilayer prepared on the surface-oxidized poly(4methyl-1-pentene) film was a substantial barrier to nitrogen penetration that was 18,000 times higher than the surface-oxidized poly(4methyl-1-pentene) film. However, the polyelectrolytes cannot stop the small gas molecules. Therefore, the natural clay of montmorillonite (MMT) was added to the polyelectrolyte multilayers of PEI/PAA. It was found that this multilayer structure was a strong barrier ability to the small gas molecules including hydrogen and helium [135]. This strong barrier property resulted from the tortuous pathway made by the flake structure MMT. With the discovery of graphene, its high aspect ratio (the ratio of width to thickness) makes it possible to be used for barrier membrane fabrication. Grunlan et al. [36] prepared a multilayer membrane by alternative deposition of PEI and graphene oxide (GO). This membrane demonstrated a low permeation to oxygen and carbon dioxide. The theoretical pore size of graphene is 0.064 nm which ensures the minimal permeability for small atoms [136,137]. However, the functional groups of GO induced defects into the graphene layer and thus impaired the barrier property of graphene [137]. In 2014, Nair et al. [138] prepared a barrier film based on the reduced graphene oxide which removed the functional groups. This film demonstrated a super impermeability to all gasses and liquids. The exceptional property was attributed to the defect-free structure of graphene. Because most of the barrier membranes were made of the flexible polyelectrolytes, they also demonstrated the self-healing ability in a humidified environment [139].

2.4. Summary

In this chapter, different mechanisms of self-healing materials were reviewed. The self-healing materials can be divided into two general groups: intrinsic materials and extrinsic materials. The intrinsic self-healing materials depend on the reversible non-covalent bonding including the hydrogen bonding, hydrophobic interactions, and electrostatic attractions. All the non-covalent
bonding can be regarded as the physical bonding because of their reversible property. In addition, it was the reversible feature that induced the self-healing ability to the materials. However, the non-covalent bonding is weak in term of mechanical strength. Therefore, they are usually combined with the covalent networks to reach a compromise between the self-healing ability and the mechanical strength. The extrinsic self-healing materials rely on the embedded healing agent in the matrix. Their biomimetic design concept origins from the human body which can heal the wound by the nutrient delivered by the blood. However, this system is too complex to be realized at this stage because of the highly-sophisticated system of human body.

The application of self-healing materials focuses on the preparation of self-healing coating because of its ability to extend the service life of the substrate. The self-healing anticorrosion coating can provide the substrate with a prolonged corrosion protection. The research was focused on recovery of the corrosion resistance after damage. This recovery property was due to the release of corrosion inhibitors to the places where corrosive electrolyte attacked. The migration of corrosion inhibitors was usually driven by the change of pH values as the corrosion reaction will increase the pH value due to the production of hydroxyl ions. The superhydrophobic coating can provide the antiadhesive and self-cleaning property to the sample surface while the barrier membranes can be used to separate ions and molecules with different property or stop all the gas and liquid from penetration. Layer-by-Layer (LbL) played a significant role in the preparation of the self-healing superhydrophobic coating and barrier membranes because of the flexible polyelectrolytes which induced the self-healing ability to the materials. The Self-healing ability could extend the service life and save much materials and energy.
CHAPTER 3

EXPERIMENTAL METHODOLOGY

3.1. Overview

In this thesis, various techniques have been used to prepare and characterize the samples. Specifically, tensile tests have been applied to understand the elastic and viscoelastic behavior of the acrylic elastomer. Layer-by-Layer (LbL) assembly technique has been applied to prepare the self-healing multilayer coating on magnesium alloy and galvanized steel substrates. Electrochemical impedance spectroscopy (EIS) was used to determine the corrosion resistance of the samples. X-ray diffraction (XRD) has been applied to examine the structure of the crystalline materials of the samples. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) have been used to analyze the surface morphology and the chemical elements distribution in the samples. Raman spectroscopy has been used to identify the chemical bonding in the samples.

These techniques have been well developed and commercial apparatuses were used to conduct the test. However, it is necessary to understand the mechanism behind the tests to better analyze the results. Therefore, the mechanisms of these tests were discussed.
3.2. The deformation mechanism behind the tensile tests of acrylic elastomer

3.2.1. The entropic contribution to the elastomer deformation

The tensile test is a powerful tool to characterize the mechanical and viscoelastic properties of elastomers. To understand the relation between the structure and the tensile behavior of elastomers, the thermodynamics that result in the corresponding behaviors of elastomers need to be understood. Two parts contributed to the force applied to the system including the energetic part ($f_E$) and the entropic part ($f_S$). For a crystalline material, such as metals, the energetic part plays a significant role; however, for an ideal elastomer with an amorphous structure, the energetic contribution can be ignored [140]. Therefore, the deformation of elastomers is mainly entropy driven. Because the energetic contribution is ignored, the free energy change ($\Delta F$) can be written as:

$$\Delta F = -T\Delta S \quad (3.1)$$

where $T$ is the absolute temperature and $\Delta S$ is the entropy change. When an affine model is applied to the elastic deformation, the change in entropy ($\Delta S$) can be written as [140] :

$$\Delta S = -\frac{nk}{2} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \quad (3.2)$$

where $n$ is the number of molecular backbone of the elastomer, $k$ is the Boltzmann constant and $\lambda_x, \lambda_y, \lambda_z$ is the deformation ratio along the $x$, $y$ and $z$ direction, respectively. Because the volume of the elastomer is regarded as constant during the deformation [140], it can be derived that:

$$\lambda_x \lambda_y \lambda_z = 1 \quad (3.3)$$

Then the equation of (3.1) can be rewritten as:

$$\Delta F = -T\Delta S = \frac{nkT}{2} (\lambda^2 + \frac{2}{\lambda} - 3) \quad (3.4)$$

where $\lambda$ is defined as the deformation ratio and $\lambda_x = \lambda$, $\lambda_y = \lambda_z = \frac{1}{\sqrt{\lambda}}$. It can be derived that the force along the $x$ direction ($f_x$) is:

$$f_x = \frac{\partial \Delta F}{\partial L_x} = \frac{nkT}{L_{x0}} (\lambda - \frac{1}{\lambda^2}) \quad (3.5)$$

where $L_{x0}$ is the initial length along the $x$ direction and $L_x$ is the final length along the $x$ direction after deformation. The true stress made by the tensile test can be calculated as:

21
\[ \sigma_{\text{true}} = \frac{f_x}{L_y L_z} = \frac{\lambda f_x}{L_{y0} L_{z0}} = \frac{nkT}{V} \left( \lambda^2 - \frac{1}{\lambda} \right) \] (3.6)

where \( L_{y0} \) and \( L_{z0} \) are the initial length along the \( y \) and \( z \) direction and \( L_y \) and \( L_z \) are the final length along the \( y \) and \( z \) direction after deformation. If tensile strains \( (\varepsilon = \lambda - 1) \) are applied to equation (3.6), it can be derived that:

\[ \sigma_{\text{true}} = \frac{nkT}{V} \left( \frac{\varepsilon^3 + 3\varepsilon^2 + 3\varepsilon}{\varepsilon + 1} \right) \] (3.7)

When the deformation is small, it can be regarded that \( \varepsilon^3 \approx 0 \). Therefore, equation (3.7) can be rewritten as:

\[ \sigma_{\text{true}} = 3 \frac{nkT}{V} \varepsilon \] (3.8)

According to Hooke’s law, \( \sigma_{\text{true}} = E\varepsilon \) and therefore \( E = 3 \frac{nkT}{V} \). \( E \) is the Young’s modulus and \( G \) is the shear modulus, \( \nu \) is the Poisson’s ratio [141]. Because the volume of the elastomer is constant during the tensile test, the bulk modulus of the materials \( \left( \frac{E}{3(1-2\nu)} \right) \) should be infinite. Therefore, the Poisson’s ratio equals to \( \frac{1}{2} \). Because \( E = 2(1+\nu)G \), it can be derived that \( G = \frac{E}{3} = \frac{nkT}{V} \). In addition, the molar number of the elastomer \( (N) \) is \( \frac{n}{N_{AV}} \), where \( N_{AV} \) is the Avogadro’s number. Therefore, the mass density of the elastomer \( (\rho) \) can be derived as \( \rho = \frac{NM}{V} = \frac{n}{N_{AV}} \frac{M}{V} \), where \( M \) is the molecular weight. Therefore, it can be derived that:

\[ G = \frac{nkT}{V} = \frac{\rho RT}{M} = \nu kT \] (3.9)

where \( R = kN_{AV} \) is the gas constant, \( \nu = n/V \) is the number of molecular backbones per volume. Therefore, equation (3.7) can be rewritten as:

\[ \sigma_{\text{true}} = G \left( \lambda^2 - \frac{1}{\lambda} \right) = \frac{nkT}{V} \left( \lambda^2 - \frac{1}{\lambda} \right) = \frac{\rho RT}{M} \left( \lambda^2 - \frac{1}{\lambda} \right) = \nu kT \left( \lambda^2 - \frac{1}{\lambda} \right) \] (3.10)

If the functionality of the crosslinks \( (f_c) \) is considered [66], equation (3.9) can be written as:

\[ G = \frac{nkT}{V} \left( 1 - \frac{2}{f_c} \right) = \frac{\rho RT}{M} \left( 1 - \frac{2}{f_c} \right) = \nu kT \left( 1 - \frac{2}{f_c} \right) \] (3.11)
The equalities expressed in equation (3.11) are critical for understanding the relation between tensile behavior and the inner structure of the elastomer. The equalities were used in Chapter 4 and 5 to calculate the molar density of the polymer and the molar mass of the molecular chains between the crosslinks.

3.2.2. The energetic contribution to the elastomer deformation

In term of the self-healing elastomer, the energetic part also contributed to the hysteresis behavior because of the existence of reversible non-covalent bonding including the hydrogen bonding, the electrostatic interactions, and the hydrophobic associations. The energetic contribution can be calculated by [66]:

\[ U_{hys} = U_0 \nu_0 f_v \]  

(3.12)

where \( U_{hys} \) is the dissipated energy, \( U_0 \) is the average fracture energy of a non-covalent bonding, \( f_v \) is the fraction of dissociated non-covalent bonding during the loading process. When the reversible non-covalent bonding is taken into account, equation (3.10) can also be rewritten as [140]:

\[ \frac{\sigma_{true}}{\lambda^2 - 1/\lambda} = G_x + \frac{G_e}{\lambda - \lambda^{1/2} + 1} \]  

(3.13)

where \( G_x \) is the shear modulus of the crosslinked networks, and \( G_e \) is the shear modulus of the entangled networks. This equation separates the contribution from the permanent crosslinks (the covalent bonding) and the reversible crosslinks (the non-covalent bonding).

3.2.3. The experimental setup

The uniaxial tensile tests were done with the INSTRON 3366 tensile machine with a 1 KN load cell. The sample length between two jaws was 50 mm. For the hysteresis and self-healing efficiency tests, the cross speed was controlled at 100 mm/min. For the tests exploring the influence of deformation speed, the cross speeds ranged from 5 to 500 mm/min.
3.3. The assembly mechanism of layer-by-layer (LbL) technique

LbL assembly was proposed by Iler [142] in 1966 and developed by Decher [68] in 1997. LbL process is a technique which assembles two oppositely charged polyelectrolytes together via electrostatic forces [68] or hydrogen bonding [143,144]. This method has been widely applied to drug deliveries [145,146], light-responsive systems [147] and separation membranes [128,148]. The polyelectrolytes can be divided into two groups: the strong polyelectrolytes and the weak polyelectrolytes. The strong polyelectrolyte possesses permanent charges while the weak polyelectrolyte is partially charged and the degree of dissociation is highly dependent on the pH value [114,128]. Many factors influence the assembly of the polyelectrolytes including solvent, salt concentration, polymer concentration, temperature, polymer molecular weight and pH value [149,150].

3.3.1. The growth mechanism of LbL assembly of polyelectrolytes

Although multiple factors influence in the assembly of polyelectrolytes, the underlying mechanism that determines the multilayer growth is the charge compensation between the polyelectrolytes. The charge compensation (Φ) was defined as the factor that the last-added polyelectrolyte compensates the charge of the previous one [151]. Therefore, the overcompensation factor (Φ − 1) determines the growth speed of the paired polyelectrolytes as a higher overcompensation factor requires a greater amount of the counter polyelectrolyte to compensate the charge. After the final step, the additional polyelectrolyte charge is balanced by the small salt ions. The charge compensation of polyelectrolytes can be divided into two groups: the intrinsic compensation and the extrinsic compensation (Figure 3.1). The strong polyelectrolytes such as the pair of poly(diallyldimethylammonium chloride) (PDADMAC) and poly(styrene sulfonate) (PSS) usually demonstrate the intrinsic compensation which leads to a linear growth because of the tightly bound molecular chains [151]. The charge of the polyelectrolytes of intrinsic compensation is balanced by the charge of the paired polyelectrolyte without the incorporation of small salt ions [152]. However, with the increase of the salt concentration in the LbL preparing process, salt ions compete with the polyelectrolytes to pair with the oppositely charged polyelectrolytes. For instance,
the negatively charged chloride ions compete with the polyanion (PSS) to compensate the charge of the polycation (PDADMAC). As a result, the extrinsic compensation dominates the multilayer growth and leads to an exponential growth as the loosely bound molecular chains [149]. In term of the LbL assembly of two weak polyelectrolytes, at least one of them penetrates from the surface to the substrate after the deposition and diffuses out after each rinsing and further deposition of the counter polyelectrolyte. The behavior was termed as the “in-and-out” diffusion of weak polyelectrolytes [153]. Therefore, both the “in-and-out” diffusion and the extrinsic compensation result in an exponential growth of the weak polyelectrolytes such as the pair of poly(ethylene imine) (PEI) and poly(acrylic acid) (PAA) [69].

![Figure 3.1 The intrinsic and extrinsic compensation of LbL assembly](image-url)
3.3.2. The thermodynamic aspect of LbL assembly of polyelectrolytes

The charge overcompensation of the LbL assembly accompanies by the change in enthalpy (ΔH) and entropy (ΔS). The electrostatic interaction between the polycation and polyanion is the enthalpy driving force [154,155]. The re-construction and release of the small ions account for the entropy gain [156]. Because the complexation of the polyelectrolytes happens spontaneously without any energy input, there must be a negative change in free Gibbs energy (ΔG < 0). The free Gibbs energy can be written as:

\[ \Delta G = \Delta H - T\Delta S \]  

(3.14)

where T is the absolute temperature. Laugel et al. [157] proposed a theory that the linear growth of the strong polyelectrolytes usually results in an exothermic complexation reaction with a negative change in enthalpy (ΔH < 0). In addition, the release of small ions including the solvent and salt ions leads to a gain in entropy (ΔS > 0) [156]. Therefore, a negative change in the free energy can be obtained. In term of the exponential growth of the weak polyelectrolytes, the polycation/polyanion complexation usually generates an endothermic reaction with a positive change in enthalpy (ΔH > 0) [157]. It is the gain in the entropy that produces the negative change in the free energy and spontaneous assembly of the weak polyelectrolytes (Figure 3.2). Vasheghani et al. [158] found that the complexation of the weak polyelectrolytes of PEI and PAA demonstrated a positive change in both enthalpy (ΔH = 35 kcal/mol) and entropy (ΔS = 137 cal/deg/mol) at 35 degrees Celsius. This result guarantees a negative change in the free energy and agrees with the theory. This result also explains the temperature sensitivity of the assembly of weak polyelectrolytes [159,160].
3.3.3. The experimental setup

Both the poly(acrylic acid) (PAA) and poly(ethylene imine) (PEI) solutions were made to 4mg/mL. The PAA solution was tuned to a pH value of ~4.5 by 0.1 M sodium hydroxide and the PEI solution was tuned to a pH value of ~9.5 by 0.1 M nitric acid. The LbL fabrication was operated by a homemade dipping coater. The samples were alternatively dipped in the beaker of PEI, deionized water, PAA and deionized water. The dipping time for PEI and PAA was set to 300s. The time of dipping in the deionized water was set to 120s. This cycle was repeated for 5, 10, 15 or 20 times.
3.4. The analysis of corrosion mechanism by electrochemical impedance spectroscopy (EIS)

3.4.1. The electrochemical aspect of corrosion

The corrosion process can be described by two reactions: the anodic reaction and the cathodic reaction. The anodic reaction produces electrons while the cathodic reaction consumes electrons [161]. The anodic reaction in the metallic corrosion is the process of metal oxidation and can be written as:

\[ M \rightarrow M^{n+} + ne^- \] (3.15)

where \(M\) is the metal, \(n\) is the valence state of the metal oxides and \(e\) represents electrons. The cathodic reaction, it is more complex depending on the environment. If the environment is isolated from oxygen, the hydrogen evolution is the key cathodic reaction and can be written as:

\[ 2H^+ + 2e^- \rightarrow H_2 \] (3.16)

where \(H^+\) represents hydrogen ions in the corrosive environment and \(H_2\) stands for hydrogen. If the corrosive environment is exposed to air (oxygen), the oxygen reduction reaction could dominate the cathodic reaction and can be written as:

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \] (3.17)
\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \] (3.18)

where \(O_2\) represents oxygen, \(H_2O\) is water and \(OH^-\) stands for hydroxyl ions. Both equations (3.17) and (3.18) are oxygen reduction reaction. The difference is that reaction (3.17) happens in the acid environment while the reaction (3.18) exists in the basic or neutral environment. In addition, the cathodic reaction of metal reduction can also happen in the presence of metal ions. The reactions can be written as:

\[ M^{3+} + e^- \rightarrow M^{2+} \] (3.19)
\[ M^+ + e^- \rightarrow M \] (3.20)

The most fundamental principle of corrosion is that the rate of the anodic reaction equals to the rate of the cathodic reaction during the corrosion of metals [161].
3.4.2. The basics of EIS

Given the information listed above, the rate of charge transfer can define the corrosion rate of a system. When the corrosion rate is higher, the corrosion resistance is lower, and vice versa. Therefore, the corrosion resistance of a system is evaluated by measuring the corrosion rate. According to Ohm’s law, the resistance \((R)\) was defined as the ratio of the voltage \((E)\) measured at the resistor to the current \((I)\) flowing through it. However, the application of resistance is limited to one circuit element, the resistor. In a real application, a corrosion system can exhibit more complex behavior including capacitive \((C)\) and inductive \((L)\) impedances. As a result, the impedance was used to measure the ability of a circuit to resist the current. Electrochemical impedance spectroscopy (EIS) technique applies an AC potential to an electrochemical cell and measures the current through the cell. When a sinusoidal potential is applied, the resistor produces a sinusoidal current without phase shift. However, a capacitor produces a sinusoidal current leading the applied voltage in phase by \(\frac{\pi}{2}\) radians, while an inductor produces a sinusoidal current lagging the voltage in a phase by an angle of \(\frac{\pi}{2}\). In a polar coordinate system, the voltage \((E)\) and the current \((I)\) can be expressed by a complex variables’ function as:

\[
E_t = E_0 e^{j\omega t} \quad (3.21) \\
I_t = I_0 e^{j(\omega t + \theta)} \quad (3.22)
\]

where \(E_t\) is the potential at time \(t\), \(E_0\) is the amplitude of the input signal, \(I_t\) is the current at time \(t\), \(I_0\) is the amplitude of the output signal, \(e\) is the base of the natural logarithm, \(j\) is the imaginary unit, \(\omega\) is the radial frequency and \(\theta\) is the phase difference between the input voltage and the output current. The relationship between the radial frequency \((\omega)\) and the frequency \((f)\) can be written as:

\[
\omega = 2\pi f \quad (3.23)
\]

Therefore, the impedance of a circuit can be calculated as:

\[
Z = \frac{E_t}{I_t} = \frac{E_0 e^{j\omega t}}{I_0 e^{j(\omega t + \theta)}} = Re^{j\theta} \quad (3.24)
\]

For a resistor, because the phase difference \((\theta)\) equals to zero, the impedance of resistors \((Z_R)\) equals to their resistance \((R)\).
For a capacitor, there is a relation among the capacitance \( C \) and the voltage \( E_t \) and the current \( I_t \) as follow:

\[
I_t = C \frac{dE_t}{dt} = j\omega CE_0 e^{(j\omega t)}
\]  

(3.25)

Therefore, the impedance of capacitors \( Z_C \) can be written as:

\[
Z_C = \frac{E_t}{I_t} = \frac{E_0 e^{(j\omega t)}}{j\omega CE_0 e^{(j\omega t)}} = \frac{1}{j\omega C}
\]  

(3.26)

For an inductor, there is a relation among the inductor \( L \) and the voltage \( E_t \) and the current \( I_t \) as follows:

\[
E_t = L \frac{dI_t}{dt} = j\omega CLI_0 e^{(j\omega t+\theta)}
\]  

(3.27)

Therefore, the impedance of capacitors \( Z_L \) can be written as:

\[
Z_L = \frac{E_t}{I_t} = \frac{j\omega CLI_0 e^{(j\omega t+\theta)}}{e^{j(\omega t+\theta)}} = j\omega L
\]  

(3.28)

With the circuit element of resistors, capacitors, and inductors, the equivalent models discussing the EIS results of a system can be built. The EIS results are usually represented by Nyquist plots and Bode diagrams (Figure 3.3). Nyquist plots account for the impedance as the length of an arrow. The imaginary part of the impedance is shown on the Y-axis and the real part of the impedance is shown on the X-axis. The drawback of Nyquist plots is the absence of frequency. Therefore, the Bode diagrams are applied to demonstrate the relation between the impedance and the phase shift with the frequency.

With the circuit element of resistors, capacitors, and inductors, the equivalent models discussing the EIS results of a system can be built. The EIS results are usually represented by Nyquist plots and Bode diagrams (Figure 3.3). Nyquist plots account for the impedance as the length of an arrow. The imaginary part of the impedance is shown on the Y-axis and the real part of the impedance is shown on the X-axis. The drawback of Nyquist plots is the absence of frequency. Therefore, the Bode diagrams are applied to demonstrate the relation between the impedance and the phase shift with the frequency.
For the analysis of the Nyquist plots and Bode diagrams, the equivalent circuits using the elements of the resistor, capacitor and inductor need to be built. An example was shown in Figure 3.4.
$R_{solution}$ represents the resistance of the corrosive solution, for instance, the sodium chloride solution. An ideal coating is expected to demonstrate a pure capacitor behavior. However, because of the existence of defects, the corrosive electrolytes can penetrate through the coating. As a result, the coating demonstrates the behaviors of both capacitors ($C_{coat}$) and resistors ($R_{coat}$). When the corrosive electrolytes react with the substrate, there forms a double layer on the surface. The capacitance of the double layer ($C_{dl}$) and the charge transfer resistance ($R_{ct}$) are applied to identify the corrosion resistance of the system. Occasionally, inductors are also used in the equivalent
models, mostly for magnesium alloys. The existence of inductor behaviors is usually attributed to the formation of corrosion pitting [21].

3.4.3. The experimental setup

The EIS tests were conducted with an Interface 1000 potentiostat from Gamry. The samples were connected to the working electrode while a graphite sheet was connected to the counter electrode. The reference electrode was a saturated calomel electrode (SCE). The scanning frequency region ranged from $10^{-2}$ to $10^5$ Hz.

3.5. The working mechanisms of other characterization techniques

3.5.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) is usually applied to identify the structure of crystalline materials. X-ray can diffract in crystalline materials because its wavelength ($\lambda$) is the same order as the lattice spacing ($d$) of crystalline materials. The diffracted X-rays can reinforce each other only at some specific angles where the diffracted X-rays are in phase. A detector is used to collect the diffracted X-rays. This condition for X-ray reinforcement was discovered by Bragg and can be expressed as [162]:

$$n\lambda = 2dsin\theta_B$$

Equation (3.29)

All the diffraction angles of $2\theta_B$ are recorded and used to identify the crystallographic structure of materials. In this study, the XRD patterns were obtained using a Bruker D8 Discover XRD with a chromium tube. The angles of the normal scan were set to 30, 60 and 90 degrees which covered the diffraction angles ranging from 15 to 105 degrees. The scanning rate was set to 2 degrees per min.
3.5.2. **Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)**

SEM was used to observe the surface morphology of the samples and the integrated EDS was applied to analyze the elements in the samples. Electrons penetrate much shallower but are scattered stronger than X-rays because they interact with both the shell electrons and the nucleus of the sample atoms [162]. The incident electron beam can produce three primary signals including secondary electrons, backscattered electrons, and characteristic X-rays. Secondary electrons are produced on the top surface. These signals are collected to display the high-resolution image of sample surfaces. Backscattered electrons are generated in the deeper layers and are dependent on the composition of samples. These electrons can be collected to demonstrate the phase distribution of samples. The incident electrons remove the electron of the sample atom and the electron on the higher energy level drops to the low energy level with the emission of X-rays. These X-rays have specific energy characterizing different elements and therefore are collected to determine the type of elements in the sample.

In the experiments, the SEM images were taken using a HITACHI SU6600 SEM. The voltage was set to 9.0 kV for the cerium compounds coated samples. The voltage was set to 1.0 kV for the PEI/PAA coated samples to minimize the charging effect. The EDS spectrum was taken at a voltage of 9.0 kV.

3.5.3. **Raman spectroscopy**

The Raman spectroscopy was applied to identify the chemical bonding in the materials. Raman spectroscopy allows recording the energy change of the molecular vibration that is resulted from the excitation radiations. The energy is dependent on the variables including frequency ($\nu$), wavelength ($\lambda$) and wavenumber ($\tilde{\nu} = \frac{1}{\lambda}$). The frequency can be expressed as:

$$\nu = \frac{c}{\lambda} = c\tilde{\nu} \quad (3.30)$$

where $c$ is the speed of light. According to the quantum mechanics, the vibrational energy of a molecule ($E_m$) can be written as [163]:
\[ E_m = \left(V + \frac{1}{2}\right)h\nu_m \]  

(3.31) 

where \( h \) is the Planck constant, \( \nu_m \) is the vibrational frequency of the molecule, \( V \) is the vibrational energy level of the molecule which can only be changed by integer numbers. When photons interact with a molecule, the energy can be transmitted, absorbed or scattered. The energy of a photon (\( E_p \)) can be written as [163]:

\[ E_p = h\nu_p \]  

(3.32)

where \( \nu_p \) is the frequency of the photon. In a Raman spectrometer, a source of photons with the same frequency is irradiated to the sample. Because the incident photon frequency is usually greater than the frequency of the molecular vibration, it is scattered by the molecules. The scattered radiation is analyzed in the Raman spectrometer. If the collision is an elastic collision, the energy level drops back to the ground state and the molecule emits photons with the same energy as the incident photons. This scattering was defined as the Rayleigh scattering (Figure 3.5). In an inelastic scattering, the energy level of the sample molecule is changed by an amount of \( \Delta E_m \). With the collision between the photon and the molecule, the photon energy can be absorbed by the molecule and the energy level of the molecule is increased to a higher level (\( V \gg 1 \)). However, this high-energy level is not stable and drops to \( V = 1 \) state. The molecule will emit a photon with an energy less than the incident photon (Figure 3.5). As a result, the sample molecule gains energy. On the contrary, if the initial energy level of the sample molecule is higher than the final energy level, the molecule loses energy and the scattered photon has a higher energy than the incident photon. These inelastic scattering were defined as the Raman scattering. The absorbed energy can be expressed as:

\[ \Delta E_m = h(\nu_i - \nu_s) = h\Delta \nu = hc\Delta \bar{\nu} \]  

(3.33)

where \( \nu_i \) is the frequency of the incident photon, \( \nu_s \) is the frequency of the scattered photon, \( \Delta \nu \) is the frequency shift and \( \Delta \bar{\nu} \) is the wavenumber shift. This wavenumber shift is usually called as Raman shift. It is a characteristic property of the molecule and represents the vibrational wavenumber of the molecule. Therefore, the Raman spectrum is illustrated by the intensity of the Raman scattering in a range of Raman shift.
Figure 3.5 The comparison of Rayleigh scattering and Raman scattering

In this study, the Raman spectra were obtained using a Renishaw 2000 Raman Microscope. The wavelength of the laser source was 785 nm and the scattered light was dispersed with a grating of 1200 l/mm. The scattered laser light was collected by the Renishaw CCD camera. A 50X objective was chosen. The exposure time was set to 10 seconds with 1 accumulation. The laser power was 0.01 W. The glass slide was covered with an aluminum foil to remove the disturbance from silicon oxide. The sample was placed on the foil covered glass slide.

3.6. Summary

In Chapter 3, the main techniques used in this thesis were described and discussed. From the thermodynamic aspect of the elastomer, the deformation is mainly entropy driven. However, with the induction of non-covalent bonding, the energetic part also participates in the deformation behavior and leads to the self-recovery and self-healing ability of the studied material. In term of the layer-by-layer (LbL) assembly, the extrinsic compensation explained the exponential growth of the polyelectrolytes multilayer on the substrate. In addition, the exponential growth of LbL
assembly is driven by an entropy gain by the release of small ions during the assembly. Electrochemical impedance spectroscopy (EIS) techniques are primarily using electronic elements to demonstrate the corrosion behavior of the samples. The impedance of resistors, capacitors, and inductors were presented since these elements were used to create the equivalent circuits for the EIS results. X-ray diffraction (XRD) was employed in this study to identify the structure of materials. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were used in conjunction to produce information about the phase composition, texture, grain boundaries character in polycrystalline materials and chemical elements in the specimen. The present study further used Raman spectroscopy to identify the chemical bonds in the investigated materials.
CHAPTER 4

THE CHARACTERIZATION AND SELF-RECOVERY BEHAVIOR OF ACRYLIC ELASTOMER VHB4910

4.1. Overview

This chapter discussed part of the first objective of the thesis which is the analysis of the mechanical, hysteresis and viscoelastic behaviors of the acrylic elastomer. Raman and FTIR spectroscopy were used to identify the chemical structure of the studied material which is critical to the self-recovery and self-healing ability. The unidirectional tensile tests were used to determine the mechanical strength of this material. The viscoelasticity of this material was explored by varying the deformation speed and the hysteresis behavior was examined using cyclic tensile tests with different strain ranges. The sample exhibited a hysteresis behavior during the cyclic tensile tests. In addition, the hysteresis behavior was recovered after certain waiting times. The strain range and the waiting time were both proved to affect its self-recovery ability. This self-recovery ability is also discussed. The results of this chapter have been published in “F. Fan, J. Szpunar, Characterization of viscoelasticity and self-healing ability of VHB 4910. Macromolecular Materials and Engineering, 300 (2015), 99 – 106”. The Copyright and permission for reusing the context, figures, and tables of these published results have been attached in the appendix.
4.2. The characterization of the acrylic elastomer

4.2.1. The chemical structure of the acrylic elastomer

Raman and Infrared spectroscopies were applied to identify the existing chemical bonds in this acrylic elastomer. Table 4.1 gives a complete bands assignment for the samples. The FTIR spectrum was obtained from the IlluminatIR II with a 36X ATR objective. The scanning ranged from 650 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). Figure 4.1 shows the Raman peaks at the wavenumber of 2956, 2916 and 2870 cm\(^{-1}\) and the FTIR peaks at 2957, 2917 and 2867 cm\(^{-1}\) which confirmed the existence of C-H3 and C-H2 bonds in the sample [163]. These methyl structures formed the backbone and side chains of the molecular chains [163]. Both the Raman peaks at 1730 and 1703 cm\(^{-1}\) and the FTIR peaks at 1731 and 1707 cm\(^{-1}\) illustrate the existence of free and hydrogen bonded carbonyl groups (C=O) which are essential structures of acrylic materials [47]. Furthermore, the FTIR peaks at 1152 cm\(^{-1}\) and the Raman peaks at 1255 and 1160 cm\(^{-1}\) represent the in-plane bending of the C-O stretching coupled with the hydroxyl group (O-H) (Figure 4.1) [47]. The carbonyl bonds and the hydroxyl groups formed hydrogen bonding. These results confirmed the existence of essential functional groups of acrylic materials in this sample. The reversible non-covalent bonds including the hydrogen bonding and the hydrophobic associations played a significant role in the self-recovery and self-healing behaviors because of their dissociation and re-association ability [60].

Figure 4.2 shows the XRD pattern of VHB 4910 from 15° to 105°. The broad peaks centered at 30° and 60° demonstrate the amorphous structure of the sample. This structure facilitated the random association of the molecular chains and thus generated a diverse distribution of entanglements and hydrogen bonding [46]. Therefore, the amorphous structure of this material created the condition for the self-recovery and self-healing ability of this material.
Figure 4.1 Identification of the chemical bonds in VHB 4910. (a) The Raman spectrum. (b) The FTIR spectrum.
Table 4.1 Observed wavenumbers and assignment of Raman and FTIR bands

<table>
<thead>
<tr>
<th>Raman [cm$^{-1}$]</th>
<th>Infrared [cm$^{-1}$]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2956</td>
<td>2954</td>
<td>C-H3 stretching vibration [163];</td>
</tr>
<tr>
<td>2926</td>
<td>2917</td>
<td>C-H2 stretching vibration [163];</td>
</tr>
<tr>
<td>2870</td>
<td>2869</td>
<td>C-H2 stretching vibration [163];</td>
</tr>
<tr>
<td>2718</td>
<td></td>
<td>Overtone of 1446</td>
</tr>
<tr>
<td>1730</td>
<td>1731</td>
<td>C=O stretching vibration (free carboxylic) [47];</td>
</tr>
<tr>
<td>1703</td>
<td>1707</td>
<td>C=O stretching vibration (hydrogen bonded carboxylic) [47];</td>
</tr>
<tr>
<td>1663</td>
<td></td>
<td>Overtone and combination</td>
</tr>
<tr>
<td>1446</td>
<td>1459</td>
<td>CH2 scissors deformation or CH3 asymmetrical deformation [163];</td>
</tr>
<tr>
<td>1373</td>
<td>1376</td>
<td>OH deformation [39];</td>
</tr>
<tr>
<td>1333</td>
<td></td>
<td>CH2 twisting [47];</td>
</tr>
<tr>
<td>1301</td>
<td></td>
<td>CH2 wag or twisting [39];</td>
</tr>
</tbody>
</table>

Figure 4.2 The XRD pattern of VHB 4910.
<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1255</td>
<td>C-O stretching coupled with O-H in-plane bending [164];</td>
<td></td>
</tr>
<tr>
<td>1152</td>
<td>1160</td>
<td>C-O stretching coupled with O-H in-plane bending [47,163];</td>
</tr>
<tr>
<td>1116</td>
<td>1117</td>
<td>C-CH2 stretching vibration [163];</td>
</tr>
<tr>
<td>1063</td>
<td>1067</td>
<td>C-O stretching vibrations [47];</td>
</tr>
<tr>
<td>1039</td>
<td>1037</td>
<td>CH2 rocking [163].</td>
</tr>
</tbody>
</table>

4.2.2. **The tensile behavior of the acrylic elastomer**

The samples were stretched with a constant deformation speed of 100 mm/min using a tensile machine. Figure 4.3a shows that the sample was stretched to a strain greater than 9 mm/mm while the nominal tensile stress reached to ~0.56 MPa. This result agreed with the typical behavior of elastomers which can be stretched to around 10 times of its original length. In addition, there were two transitions in the strain-stress curve because the modulus varied during the loading process. The modulus of this sample was derived by taking one derivative of the strain-stress curve. Figure 4.3b shows that the modulus decreased at the low deformation range from 0 to 0.76 mm/mm and then stayed stable during the medium deformation ranging from 0.76 to 5.46 mm/mm. Finally, the modulus increased at the high deformation range from 0.76 to 9.16 mm/mm. Therefore, the tensile curve was divided into three sections with a softening point and a hardening point at the low strain of 0.76 mm/mm and the high strain of 5.46 mm/mm, respectively. The softening behavior was due to the dissociation of reversible non-covalent bonding which played a more important role in the low deformation range [17]. Because the entropic force contributed most to the deformation of elastomers, the hardening behavior was attributed to the finite chain extensibility at the high deformation range where the entropy experienced a rapid loss [140]. In addition, stress-induced crystallization also contributed to the hardening transition [165].
Figure 4.3 The tensile test of VHB 4910. (a) The strain-stress curve under a deformation speed of 100 mm/min. (b) The modulus and the division of the strain-stress curve.
4.2.3. The deformation speed effect on the tensile tests

This material also exhibited a viscoelastic behavior because it was found that the strain-stress response was dependent on the deformation speed. The viscoelasticity resulted from the synergistic interactions between the covalent bonds and non-covalent bonding. The strong covalent bonds at the crosslinks deformed elastically to accommodate the deformation when the force was applied, while the reversible non-covalent bonding is weaker and dissociated under the tensile force. The dissociation of the non-covalent bonding depended on the deformation speed and thus induced the viscous-like property of the material. Figure 4.4 shows that the fracture stress r from ~0.29 to ~0.70 MPa when the deformation speed rose from 5 to 500 mm/min. When the deformation speed was low, the non-covalent bonds had enough time to slip and break. However, when the deformation speed increased, they cannot respond to the deformation in time. Therefore, the material required a larger force to be stretched to the same strain when the deformation speed was higher.

![Figure 4.4 The strain-stress curves under different deformation speed.](image-url)
The non-affine tube model was applied to separate the viscous and elastic contribution to the mechanical strength [140]. This model defines the relation between mechanical parameters given by equation (4.1):

\[
\frac{\sigma_{nom}}{\lambda - 1/\lambda^2} = G_x + \frac{G_e}{\lambda - \frac{1}{\lambda^2} + 1}
\]  

(4.1)

where \( \lambda \) is the deformation ratio (deformed length between the jaws/original length between the jaws), \( \sigma_{nom} \) is the nominal tensile stress, \( G_x \) is the shear modulus of the crosslinked networks, and \( G_e \) is the shear modulus of the entangled networks. This model separated the contribution from crosslinks and entanglements. Figure 4.5 shows that \( G_x \) fluctuated around an average value of 9.76 kPa over different deformation speeds as the molecular chains between the crosslinks deformed elastically before the specimen fractured while \( G_e \) increased with the deformation speed. This increase of \( G_e \) confirmed that the dissociation of the entanglements was dependent on the deformation speed and responsible for the viscoelasticity of the acrylic elastomer.

Figure 4.5 The deformation speed dependency of the shear modulus of crosslinked networks (\( G_x \)) and the shear modulus of entangled networks (\( G_e \)).
4.2.4. The hysteresis behavior of the acrylic elastomer

In addition to the dependency of the deformation behavior on the deformation speed, another typical behavior is the hysteresis behavior. Cyclic tensile tests were used to study the hysteresis behavior of the samples. The hysteresis loop was defined as the difference between the strain-stress curves of loading and unloading processes when the samples were exposed to cyclic tensile tests (Figure 4.6a). The area in the hysteresis loop was defined as the hysteresis area. The hysteresis area existed throughout all the deformation ranges and increased from ~0.04 to ~0.28 MJ/m$^3$ when the tensile strain increased from 2 mm/mm to 8 mm/mm (Figure 4.6b). The results indicate that the dissociation of non-covalent bonding existed over the whole deformation range and more cross-links were fractured with the stretching of the samples. Energy dissipation ratio was used to study the effect of different strains on the hysteresis behavior. The energy dissipation ratio was defined as the ratio of the hysteresis area to the toughness of the sample. The toughness was defined as the area under the loading curve and represented the work input to stretch the sample [166]. Figure 4.6b shows that the energy dissipation ratio decreased from ~30% to ~22% when the tensile strain increased from 2 mm/mm to 8 mm/mm. This decrease was due to that the non-covalent bonding is weaker than the covalent bonding and thus more energy was stored by the elastic deformation of the molecular chains.

The amount of the fractured non-covalent bonding can be calculated by equation (4.2) [62]:

$$U_{hys} = U_0 \nu_0 f_v$$  \hspace{1cm} (4.2)

where $U_{hys}$ is the dissipated energy, $U_0$ is the average fracture energy of a non-covalent bonding which is assumed to be on the order of 10$^2$ kJ/mol [167,168], $f_v$ is the fraction of dissociated non-covalent bonding during the loading process and $\nu_0$ is the molar density of the networks between the crosslinks. The molar density ($\nu_0$) can be calculated from the equation (4.3) [140]:

$$G_x = \nu_0 RT \left(1 - \frac{2}{f}\right)$$  \hspace{1cm} (4.3)

where $R$ is the gas constant, $T$ is the absolute temperature, and $f$ is the functionality of the crosslinks. Assuming a phantom network [60,62,165], the functionality of the crosslinks is 3 because of the crosslinking structure of acrylic materials. Therefore, the molar density of the networks between the crosslinks was derived to be ~11.82 mol/m$^3$. With this result, it was obtained
that the fraction of dissociated non-covalent bonding increased from ~3.5% at a strain of 2 to ~23.5% at a strain of 8 (Figure 4.7).

Figure 4.6 Analysis of the hysteresis behavior of VHB 4910. (a) The hysteresis area increases with the tensile strain. (b) The hysteresis area and the energy dissipation ratio shown as a function of the tensile strain.
The strain dependence of self-recovery ability

Successive cyclic tensile tests were used to confirm the existence of reversible non-covalent bonding in the materials. The difference between the rupture of non-reversible covalent bonding and the dissociation of reversible non-covalent bonding is the recovery ability as the rupture of covalent bonding is a permanent break to the sample while the dissociation of non-covalent bonding is a temporary break which can recover when the force is released [7,58]. The two-successive cyclic tensile tests were conducted with tensile strains from 2 mm/mm to 8 mm/mm. There was a waiting time of 60 min between the two loading-unloading processes. Figure 4.8a shows that the second cyclic tensile tests almost followed the first path with a strain of 2 mm/mm. This behavior was different from the observation of double network gels which formed permanent damage to the sacrificial networks [57]. This result confirmed the existence of reversible non-covalent bonding in the sample. In addition, the second loading-unloading cycle of the sample that was stretched to 8 mm/mm only recovered part of the hysteresis loop after 60 min because more
non-covalent bonding was ruptured with higher strains and thus took more time to recover to the original state. The ratio of the area of the second hysteresis loop to that of the first hysteresis loop was defined as the hysteresis ratio. The hysteresis ratio was employed to evaluate the self-recovery efficiency. Figure 4.8b shows that the self-recovery efficiency was around 98% when the tensile strain was less than 4 mm/mm, but decreased to 85% when the tensile strain increased to 8 mm/mm.

Figure 4.8 Measurement of the self-recovery ability of VHB 4910. (a) The two hysteresis loops between 60 min of two cyclic test at a strain of 2 mm/mm and 8 mm/mm, respectively. (b) The self-recovery ability decreased with the increase of tensile strains.
4.3.2. The time dependence of self-recovery ability

Because the self-recovery ability is time dependent, successive cyclic tensile tests were applied to the samples with different waiting times. The samples were first stretched to a strain of 6 mm/mm with a strain rate of 100 mm/min and then released with the same speed. With a waiting time of 0.25, 1, 5, 30, 60 and 120 minutes, the samples were loaded and unloaded with the same process. Figure 4.9 demonstrates the recovery behavior of the samples under different waiting times. With a waiting time of 0.25 min, the sample recovered more than 50% of the hysteresis loop (Figure 4.9a). With the increase of the waiting time, the area of the second hysteresis loop increased. The two hysteresis loops overlapped each other when the waiting time reached 60 min (Figure 4.9e). Figure 4.10 shows that the hysteresis ratio increased from ~53% to ~96% when the waiting time increased from 0.25 to 120 min. The residual strain was defined as the remaining strain before the second loading-unloading cycle. The recovery of residual strains can also illustrate the recovery behavior of the samples as the beak of covalent bonding results in a permanent residual strain [74]. The residual strain of the investigated material decreased from ~0.26 to ~0.02 mm/mm with the increase of waiting times (Figure 4.10). The samples recovered more than 90% during the first 30 min while took another 90 min to recover the remaining 10% residual strain. This was due to the competition of the entropic gain of the molecular backbones and the re-association of the non-covalent bonding. When the force was released, the number of the status of the molecular backbones increased and the increase leads to the entropy gain. However, when the non-covalent bonding re-associated, the confined number of states of the molecular backbones constrained the entropy gain. The deformation of elastomers is mainly driven by the entropic forces, compared with the crystalline metals of which the energetic force is more important [140]. Therefore, when the force was released, the restore of entropy was dominant at high strains leading to the fast recovery as the non-covalent bonds were ruptured. However, the non-covalent bonding re-associated at the small deformation and slowed down the recovery [17].
Figure 4.9 The time dependency of self-recovery ability. (a) The hysteresis recovered after 0.25 min. (b) The hysteresis recovered after 1 min. (c) The hysteresis recovered after 5 min. (d) The hysteresis recovered after 30 min. (e) The hysteresis recovered after 60 min. (f) The hysteresis recovered after 120 min.
Figure 4.10 The hysteresis ratio and residual strain as a function of waiting time

4.4. Summary

Raman and Fourier transform infrared (FTIR) spectroscopy were used to identify the chemical structure of the studied material. The existence of methyl groups (-CH2) formed backbones and side chains of the materials. The carbonyl bonds (C=O) and the hydroxyl groups (-OH) provided the condition for hydrogen bonding. All the above chemical bonds are essential for the acrylic materials.

The mechanical, hysteresis and viscoelastic behaviors of this material were tested using tensile tests. The unidirectional tensile tests confirmed the excellent extensibility of this material which was extended to a strain around 9 mm/mm before the break. In addition, the tensile stress increased with the deformation speed. The dependency of the strain rate origins from the synergistic interactions between the covalent bonding and non-covalent bonding. This result confirmed the
viscoelasticity of the material. Furthermore, the hysteresis behavior existed throughout all the tensile strains as the hysteresis area increased with the tensile strains.

The cyclic tensile tests were applied to confirm the self-recovery ability of the materials. The self-recovery ability was confirmed and found to be dependent on both the tensile strains and the waiting time between two cyclic tensile tests. More non-covalent bonding broke when the deformation strain increased. Therefore, it required more time to recover after the deformation with a larger strain. The competition between the entropy gain of the molecules and the re-association of the non-covalent bonding led to the fast recovery in the first 30 minutes and the slowed recovery after that.
CHAPTER 5

THE SELF-HEALING BEHAVIOR AND MECHANISM OF ACRYLIC ELASTOMER VHB 4910

5.1. Overview

This chapter focused on the self-healing ability and mechanism of the acrylic elastomer. As the self-recovery behavior of VHB 4910 was observed using the cyclic tensile tests in Chapter 4, the self-healing behavior was further examined in this chapter. Compared with the self-recovery behavior, the self-healing behavior healed the damages made on the samples. Therefore, the samples were cut and the self-healing ability was examined. The self-healing ability of the samples was found to be dependent on the healing time and the healing temperature.

Because the reversible non-covalent bonding played a significant role in the self-recovery behavior, it was hypothesized that the hydrogen bonding was also essential to the self-healing ability. Raman spectroscopy was applied to discover the influence of hydrogen bonding on the samples by scanning different points along a line which was vertical to the cutting interfaces. Furthermore, a theoretical model was used to confirm that the chain diffusion process also contributed to the self-healing ability.
In summary, this chapter examined the time-dependent and temperature-dependent self-healing behavior of the acrylic elastomer and explained its self-healing mechanism including the re-association of hydrogen bonding and the diffusion of the molecular chains. The results of this chapter have been published in “F. Fan, J. Szpunar, The self-healing mechanism of an industrial acrylic elastomer. Journal of Applied Polymer Science, 132 (2015), 42135”. The Copyright and permission for reusing the context, figures, and tables of these published results have been attached in the appendix.

5.2. Characterization of the self-healing behavior

5.2.1. The tensile test setup

All of the samples were prepared with a dimension of 25.4 × 0.889 × 100 mm³. Figure 5.1a shows that the sample was cut in the middle using a scalpel and brought into contact manually. Then, the samples were kept in the ambient environment before the tensile tests. The healed samples were held by the claws on the two ends and stretched with a constant deformation speed of 100 mm/min during the tensile test (Figure 5.1b). Three tests were done for each healing time and temperature. The samples demonstrated an autonomous self-healing ability without any energy input.

5.2.2. The time-dependent self-healing ability

It was found that the healed samples were stretched to different strains depending on the healing time. To evaluate the effect of healing time on the self-healing ability, the samples were kept at the ambient temperature for a healing time ranging from 10 to 960 minutes before the tensile test. Then, the healed samples were stretched at a constant strain rate of 100 mm/min. Figure 5.2a shows that both the nominal fracture strain and fracture stress respectively increased from an average value of ~468% and ~0.18 MPa to an average value of ~727% and ~0.30 MPa with the healing time increasing from 10 minutes to 240 minutes. The nominal fracture strain and fracture stress leveled off after that and finally reached to ~760% and ~0.35 MPa after a healing time of 960 minutes. Moreover, the samples healed after 960 minutes at room temperature reached to ~84% of the nominal tensile strength of the original samples (Figure 5.2b). Its fracture stress and fracture
strain were respectively ~0.43 MPa and ~850% which was rather close to ~0.56MPa and ~9 mm/mm of the original samples. The deviation from the average value existed mainly because this material was notch sensitive and the contact of the cut specimens cannot be guaranteed to be perfect and small notches may nucleated the early failure.

Figure 5.1 The self-healing experiment of VHB 4910. (a) The sample was cut in the center and brought together manually. (b) The healed sample before and during a tensile test.
The area under the strain-stress curve was defined as toughness which measured the work done by the tensile machine during the loading process. The material was very tough as its toughness was ~1.91 MJ/m³ which was almost twice of the value (~1 MJ/m³) of the copolymer of acrylamide and acrylate [60]. The self-healing ability of this material was evaluated using the term of healing efficiency which was determined by the ratio of the toughness of the healed sample to that of the original sample [18]. Figure 5.2c shows that the self-healing efficiency increased from ~29% to ~60% when the healing time rose from 10 to 240 minutes. Finally, the self-healing efficiency gradually grew to an average value of ~69% with a healing time of 960 minutes. Therefore, the self-healing process of this material under room temperature was divided into two steps where the samples healed fast in the first 240 minutes while slowed down in the rest time. This result agreed with the self-recovery behavior of this material which was observed by the cyclic tensile tests in Chapter 4. In a relatively short healing time, the toughness of healed samples recovered to ~1.32 MJ/m³ which was much higher than other self-healing materials [18,64].

Because the cutting interfaces were expected to approach an equilibrium state after which the ability of self-healing was lost [45], the influence of waiting time on the self-healing ability was tested. Here, the waiting time described the period between cutting and contacting the samples. However, this material exhibited an impressive self-healing ability even after a waiting time of 40 hours. Figure 5.3 shows that after the same healing time of 120 minutes, the fracture strain and stress of the healed samples with a waiting time of 40 hours decreased only by ~11% to ~5.84 mm/mm and ~0.23 MPa in comparison to the samples that were joined just after they were cut and separated (~6.57 mm/mm and ~0.26 MPa). But this weakened strength also indicates that the self-healing samples materials had a maximum waiting time.
Figure 5.2 The self-healing test results under room temperature. (a) The fracture strain and stress increase with the healing time. (b) The best healed sample under room temperature. (b) The self-healing efficiency increases with the healing time.
5.3. Determination of the self-healing mechanism

Because the existence of the hydrogen bonded carbonyl bonds was observed in the Raman and FTIR spectra (Figure 4.1), it was assumed that hydrogen bonding contributed to the self-healing ability of the materials [66]. In addition, both self-recovery and self-healing processes had two recovering and healing stages. The chain diffusion process could also contribute to the self-healing behavior in the slow recovering and healing stage [4].
The role of hydrogen bonding in self-healing

As the carbonyl bond (C=O) was likely responsible for hydrogen bonding with the hydrogen atom of hydroxyl groups, it was important to test the Raman spectrum from 1665 to 1780 cm\(^{-1}\) including the hydrogen bonded and free carbonyl bands. Raman spectroscopy was used to observe the carbonyl bands at different spots of the healed samples. Specifically, the carbonyl bands were recorded along a line which was 14 micrometers long starting from the cutting interfaces to the area that was not affected by the cut. Figure 5.4 illustrates the variation of the Raman spectra. The intensity of the Raman spectrum increased continuously with the distance from 0 to 14 microns away from the cutting interfaces. At the spots closing to the cutting interfaces, most of the carbonyl bonds were damaged and thus cannot be detected. The peak intensity doubled around the cut when the detector moved to the spots at 2 microns from the cutting interfaces. The intensity grew five times at the spot which was 4.5 microns from the cut and finally reached to seven times at the spot.

Figure 5.4 The Raman spectrum of the carbonyl bands along a scanning line perpendicular to the cutting interfaces.

5.3.1. The role of hydrogen bonding in self-healing

As the carbonyl bond (C=O) was likely responsible for hydrogen bonding with the hydrogen atom of hydroxyl groups, it was important to test the Raman spectrum from 1665 to 1780 cm\(^{-1}\) including the hydrogen bonded and free carbonyl bands. Raman spectroscopy was used to observe the carbonyl bands at different spots of the healed samples. Specifically, the carbonyl bands were recorded along a line which was 14 micrometers long starting from the cutting interfaces to the area that was not affected by the cut. Figure 5.4 illustrates the variation of the Raman spectra. The intensity of the Raman spectrum increased continuously with the distance from 0 to 14 microns away from the cutting interfaces. At the spots closing to the cutting interfaces, most of the carbonyl bonds were damaged and thus cannot be detected. The peak intensity doubled around the cut when the detector moved to the spots at 2 microns from the cutting interfaces. The intensity grew five times at the spot which was 4.5 microns from the cut and finally reached to seven times at the spot.
14 microns from the cut. These results confirmed the decrease of the chemical bonds at the cutting interfaces because of the cut.

Figure 5.5 The analysis of the Raman spectrum. (a) The $2^{nd}$ derivation of the Raman spectrum of the carbonyl bands. (b) The Lorentz fitting of the Raman spectrum of the carbonyl bands.
To quantify the hydrogen-bonded carbonyl bonds and free carbonyl bonds at different spots, two derivatives of the Raman spectra were calculated. The second derivative plot of the Raman spectra indicates that there were two peaks in the carbonyl bands at the wave number of 1699 and 1730 cm\(^{-1}\) (Figure 5.5a). The peak at 1730 cm\(^{-1}\) represented the free carbonyl bonds while the peak at 1699 cm\(^{-1}\) was associated with the hydrogen-bonded carbonyl bonds [47]. Lorentz function was applied to fit the Raman spectra to separate these two peaks. Figure 5.5b shows that the combined carbonyl bands were separated into two bands including the free carbonyl bands and the hydrogen bonded carbonyl bands. The fitted bands followed the spectrum of the raw bands and confirmed the good fitting.

The wavenumber and full width at half maximum (FWHM) of the fitted carbonyl bonds at different spots were compared. Figure 5.6a shows that the band wavenumber of the hydrogen-bonded carbonyl bonds increased with the distance at first, but leveled off from the distance of 2 to 14 micrometers, while the FWHM of the hydrogen-bonded carbonyl bonds decreased with the distance at first but also leveled after 2 micrometers. The hydrogen bonding constrained the vibration of original carbonyl bonds and thus the wavenumber decreased and the FWHM of the corresponding chemical bonds broadened [47]. The result confirmed that there existed strong hydrogen bonding at the cut interface which re-associated both parts. Compared with the hydrogen-bonded carbonyl bond, the band wavenumber and FWHM of the free carbonyl bond remained almost constant with the distance from 0 to 14 micrometers (Figure 5.6b). In addition, the damage of the cut brought a stress field around the cut interfaces. The cut damage and the stress field reduced both the hydrogen bonded carbonyl bonds and the free carbonyl bonds. Figure 5.6c shows that both the Raman intensities of the hydrogen bonded and the free carbonyl bonds decreased with the distance closer to the cut interfaces. However, the intensity ratio of the hydrogen-bonded carbonyl bonds to the free carbonyl bonds increased when the distance was closer to the cut interfaces. This increased ratio confirmed that some free carbonyl bonds transferred to the hydrogen bonded carbonyl bonds at the cut interfaces because the original structure was broken and more carbonyl bonds were available for forming the hydrogen bonding.
Figure 5.6 The variation of the carbonyl bands with respect to the distance from the cutting interfaces. (a) The change of wavenumber and FWHM of the hydrogen bonded carbonyl bonds with the distance from the cutting interfaces. (b) The change of the wavenumber and FWHM of the free hydrogen bonded carbonyl bonds with the distance from the cutting interfaces. (c) The Raman intensity and intensity ratio of the two carbonyl bonds change with the distance from the cutting interfaces.
To confirm that the hydrogen bonding contributed to the self-healing process, tensile tests were applied to the urea immersed samples. As urea solution is known to be a chemical which can disrupt hydrogen bonding [169], the fresh cut interfaces were immersed into a 30 wt.% urea solution for 1 minute and then brought the interfaces into contact for 30 minutes. The fracture strain and stress of the urea-processed samples were reduced respectively to ~208% and ~0.11 MPa. Compared with the mechanical strength (~5.26 mm/mm and ~0.20 MPa) of the healed samples without immersing in the urea solution, the fracture strain and stress were only half of the values (Figure 5.7). Therefore, hydrogen bonding was verified to be one of the self-healing mechanisms of the acrylic elastomer.

Figure 5.7 The comparison of the fracture strain and stress with and without the urea treatment after a healing time of 30 minutes.
5.3.2. The chain diffusion effect on self-healing

According to Wool et al. [170], the chain diffusion process also affected the self-healing behavior and the true fracture stress of the healed samples ($\sigma_{tr}$) was proportional to $t/M_x^{0.25}$, where $t$ is the healing time, $M_x$ is the molar mass of the molecular chains between the crosslinks. The molar mass of the molecular chains between the crosslinks could be calculated by the equation (5.1) as [140]:

$$G_x = \frac{\rho RT}{M_x} \left(1 - \frac{2}{f}\right)$$  \hspace{1cm} (5.1)

where $\rho$ is the density of the acrylic elastomer which is measured to be 1.165 g/cm$^3$. Based on the calculated $G_x$ of 9.76 kPa in Chapter 4 and the phantom network where $f$ is 3, the molar mass between crosslinks ($M_x$) was derived to be around 98,580 g/mol. Therefore, the true fracture stress ($\sigma_{tr}$) was derived to be proportional to the healing time ($t$) and expressed the relationship as follows:

$$\log_{10} \sigma_{tr} = C + 0.25 \log_{10} t$$  \hspace{1cm} (5.2)

where $C$ is a constant decided by the material. As this material is an elastomer, the volume change during tensile tests was ignored [171]. Therefore, the true fracture stress $\sigma_{tr}$ was calculated by:

$$\sigma_{tr} = \lambda \cdot F/A_{in}$$  \hspace{1cm} (5.3)

where $\lambda$ is the deformation ratio (deformed length/initial length), $F$ is the force, and $A_{in}$ is the initial cross section area. Figure 5.8 shows that the relationship between the true fracture stress of the healed samples and the healing time in the double-logarithmic coordinates. The data were fitted with a general linear equation and the slope was extracted to be 0.25 with a standard deviation of 0.017. Such an agreement with the theory indicates that the chain diffusion process contributed to the self-healing behavior and accounted for the time-dependence of the healing process.
Figure 5.8 The proportional relationship between the true fracture stress of healed samples and the healing time in double-logarithm coordinates.

Raman spectra of two different points on the sample were also recorded after different healing times from 10 to 240 minutes. One of the points was close to the line of cut while another was 30 micrometers from this line. Figure 5.9a shows that the intensity of the spectra for the point close to the cut increased with the time of healing. This behavior was attributed to the chain diffusion which facilitated molecular chains crossing the cut interfaces. With the increase of time, more molecular chains entangled and more hydrogen bonds re-associated. The entanglement and re-association led to the decrease of the chains mobility [4]. Therefore, the intensity increased significantly during the first 120 minutes, while the increase in that time was negligible. The ratio of the areas under the Raman spectra of the healed samples to that of the original sample was applied to quantify the recovery efficiency of the Raman spectrum. Figure 5.9b shows that the recovery efficiency increased fast from \(~44\%\) to \(~90\%\) when the healing time increased from 10 to 120 minutes. However, the recovery slowed down and finally reached to \(~94\%\) after a healing
time of 240 minutes. On the contrary, the spectra of the point on the original surface stayed consistent from 10 to 240 minutes as it was too far to be affected by the chain diffusion process (Figure 5.9c).

Furthermore, Flory’s theory indicates that the mobility of molecular chains increased with the temperature [172]. The healing ability of this material was tested under different healing temperatures from 25 to 120 degrees Celsius with the same healing time of 120 minutes. The healed samples were kept in the furnace after it reached to the desired temperature. Figure 5.10a shows that the strain-stress curve of the healed samples followed the same path but broke at different strains. Generally, the mechanical strength increased with the healing time. The sample healed under 80 degrees Celsius demonstrated almost the same strain-stress curve as the original sample. Furthermore, the mechanical strength of the sample that was healed under 120 degrees Celsius surpassed that of the original sample. Figure 5.10b shows that the fracture strain increased with the healing temperature and the fracture stress demonstrated almost a proportional relation to the healing temperature. The mechanical strength of the samples increased from ~6.57 mm/mm and ~0.26 MPa for the samples healed under room temperature to ~9.80 mm/mm and ~0.67 MPa for the samples healed under 120 degrees Celsius for 120 minutes. This excellent mechanical strength was even higher than the values of the original samples (~9 mm/mm and 0.56 MPa). The healing efficiency was defined as the ratio of the toughness of the healed samples under different healing temperatures to that of the original samples. As a result, the healing efficiency increased from ~49% for the samples healed under room temperature to ~123% for the samples healed at 120 degrees Celsius (Figure 5.10c). The healing efficiency also illustrated a linear relationship with the healing temperatures. This significant improvement of self-healing ability was attributed to the high temperature which injected more energy into the healing process and promoted the chain entanglement at the cutting interface.
Figure 5.9 The Raman spectra of the carbonyl bands with different healing time. (a) The Raman spectra of the carbonyl bands at the cutting interfaces with different healing times. (b) The Raman intensity increases with the healing time. (c) The Raman spectra of the carbonyl bands at a pristine spot.
Figure 5.10 The effect of temperature on the healing behavior. (a) The strain-stress curve of healed samples with different healing temperature. (b) The fracture strain and stress increase with the healing temperature. (c) The healing efficiency increases with the healing temperature.
Thus, the self-healing mechanism of the acrylic elastomer was attributed to two factors: (1) the re-association of the hydrogen bonding; (2) the chain diffusion process. Figure 5.11 demonstrates the self-healing process of this material. When the separated parts of this material were brought together, the dangling carbonyl bonds from one part re-associated with the carbonyl bonds from the other part and stuck the cutting interfaces together. The hydrogen bonding played a role as a bridge which created the condition for the chain diffusion. The molecular chains diffused into the other part and entangled with the molecular chains in the other part to form the entanglements which enforced the self-healing ability of this material. Therefore, two self-healing stages were observed in the self-healing tests.

![Diagram of self-healing mechanism](image)

Figure 5.11 The scheme of the self-healing mechanism of the acrylic elastomer.

### 5.4. Summary

In this chapter, it was found that the self-healing ability of VHB 4910 increased with the healing times and reached to a comparatively high self-healing efficiency under room temperature. In addition, the mechanical strength of the healed samples only dropped by ~11% with a waiting time of 40 hours. The studied material demonstrated a better self-healing ability than the samples that lost the self-healing ability in a short waiting time.
It was found that the re-association of hydrogen bonding initiated the self-healing process because the wavenumber of the hydrogen bonded carbonyl bonds decreased while the full width at half maximum (FWHM) of the hydrogen bonded carbonyl bonds broadened when the scanning spot was closer to the cutting interfaces. The drop of the mechanical strength of the urea treated samples further confirmed the effect of hydrogen bonding on the self-healing behavior.

Furthermore, the proportional relationship between the true fracture stress and the healing time was established. This relationship proves that the chain diffusion process also contributed to the self-healing ability. In addition, the higher temperature induced a better healing efficiency as the healing process was promoted by the energy input.
CHAPTER 6

THE POLY(ETHYLENE IMINE)/POLY(ACRYLIC ACID) (PEI/PAA) MULTILAYERS SELF-HEALING COATING ON MAGNESIUM ALLOY AZ31

6.1. Overview

One of the most significant applications of self-healing materials is self-healing coating as it can extend the service life of the substrate. Magnesium alloy AZ31 was chosen as the substrate. This alloy has been applied to various applications including the automotive industry, electronics, aerospace and biomedical applications because of its high strength to weight ratio, high damping capacity and degradable property which is necessary for biomedical applications [21–26]. Our original plan was applying the acrylic elastomer directly to the magnesium alloy substrate. However, it cannot be dissolved in various solvents. As a result, the poly(acrylic acid), which has a similar structure as the acrylic elastomer, was chosen to be coated on the magnesium alloy.

Because of the sensitivity of magnesium alloy, a cerium conversion layer was needed to be prepared on the substrate before the polymeric coating was deposited. The cerium-based conversion layer was applied to improve the corrosion resistance of magnesium alloys and the adhesion between the substrate and the polymeric top coatings [173]. After that, the poly(ethylene...
imine) (PEI) and poly(acrylic acid) (PAA) were alternatively deposited on the cerium conversion layer using layer-by-layer (LbL) assembly.

In this Chapter, the preparation of the multilayer coating and the characterization of the corrosion resistance and self-healing ability were discussed. Part of the results of this chapter has been published in “F. Fan, C.Y. Zhou, X. Wang, J. Szpunar, Layer-by-Layer assembly of a self-healing anticorrosion coating on magnesium alloys. ACS Applied Materials & Interfaces, 7 (2015), 27271 – 27278”. All the experiments were designed and conducted by Fan Fan. The manuscript was written by Fan Fan. The graphene oxide was prepared by Chunyu Zhou. The manuscript was reviewed and corrected by Xu Wang and Jerzy Szpunar. The Copyright and permission for reusing the context, figures, and tables of these published results have been attached in the appendix.

6.2. Preparation and characterization of the PEI/PAA multilayers coating

6.2.1. Preparation of the cerium conversion layer

The AZ31 samples were ground with the #1200 SiC paper. The surface morphologies of the samples were observed using SEM. Figure 6.1a shows the scratched surface after the grinding. Then, the sample was immersed in a 0.05 M cerium nitrate solution for 20 min. The cerium compounds formed small particles on the surface (Figure 6.1b). However, it was expected to produce a continuous layer of cerium compounds on the surface and the small particles cannot provide sufficient protection to the substrate. As a result, the immersion time was increased to 30 min. Figure 6.1c shows that a continuous cerium conversion layer formed on the surface with minor cracks. This sample was denoted as Ce(III)&Ce(IV). To evaporate the water molecules and further oxide $Ce^{3+}$ to $Ce^{4+}$, the sample of Ce(III)&Ce(IV) was sintered at 80 degrees Celsius for 30 min to obtain the sample of Ce(IV) (Figure 6.1d).

Magnesium alloys are sensitive in the cerium nitrate solution. When the sample was immersed in a 0.05 M cerium nitrate solution, the magnesium dissolved at the anode while transferred electrons ($e^-$) to the cathode. As a result, the dissolved oxygen was reduced to hydroxyl ions ($OH^-$). The oxidation at the anode and reduction reaction at the cathode were as follows:

$$Mg \rightarrow Mg^{2+} + 2e^-$$  \quad (6.1)
With the increase of the concentration of hydroxyl ions at the surface, the $OH^-$ reacted with magnesium ($Mg^{2+}$) and cerium cations ($Ce^{3+}$) to form a layer of Mg(OH)$_2$ and Ce(OH)$_3$ on the surface. Part of the Ce(OH)$_3$ was further oxidized to CeO$_2$ [117,174].

Figure 6.1 The SEM images of the cerium conversion layers. (a) The bare AZ31 polished with #1200 SiC paper. (b) The cerium conversion layer after immersion in 0.05 M cerium nitrate for 20 min. (c) The cerium conversion layer after immersion in 0.05 M cerium nitrate for 30 min. (d) The cerium conversion layer after immersion in 0.05 M cerium nitrate for 30 min and sintered at 80 degrees Celsius for 30min.

6.2.2. Preparation of the PEI/PAA multilayers

To prepare the PEI/PAA multilayers on the cerium conversion layer, the sample of Ce(IV) was immersed in the solution of PEI for 5 min. The pH value of PEI was tuned with nitric acid to 9.5 to obtain the positive charges. Because the isoelectric point (IEP) of CeO$_2$ ranges from 5.2 to 6.75 [175,176], the cerium-based conversion layer showed a negatively charged property in the PEI
solution. Therefore, the positively charged PEI adhered to the cerium-based conversion layer via the electrostatic attractions. The sample was then washed with deionized water for 2 min to wash off the residual PEI. After that, the sample was immersed in the solution of PAA. The pH value of the PAA solution was tuned to 4.5 which was larger than the acid dissociation constant (4.3 – 4.4) of the carboxylic group (-COOH) necessary to ionize PAA [35]. The deprotonated PAA possessed negative charges and therefore bound with the positively charged PEI. Finally, the sample was washed with deionized water for 2 min to remove the residual PAA. This deposition cycle was repeated for 10 and 20 times to obtain the final products of Ce(IV)/(PEI/PAA)10 and Ce(IV)/(PEI/PAA)20. Figure 6.2 illustrates the multilayer structure of the coating on the AZ31 substrate.

Figure 6.2 The multilayer structure of the multilayers coating
Figure 6.3 The XRD pattern and Raman spectra of the multilayer coatings. (a) The XRD pattern. (b) The Raman spectra.
6.2.3. Characterization of the PEI/PAA multilayers

X-ray diffraction (XRD) and Raman spectroscopy were applied to define the composition of the composites formed. It was found that the peaks at 2theta of 43, 50, 73 and 89 degrees represented the cerium dioxide (CeO$_2$), while the peaks at 2theta of 41, 75 and 88 degrees represented the cerium hydroxide (Ce(OH)$_3$) (Figure 6.3a). These peaks confirmed the deposition of Cerium compounds on the surface. Figure 6.3a shows that after sintering the sample the peaks at 2theta of 41 and 88 degrees which represented the Ce(OH)$_3$ disappeared. This was due to the further oxidation of Ce(III) to Ce(IV) which transformed Ce(OH)$_3$ to CeO$_2$. The samples of Ce(IV)/(PEI/PAA)10 and Ce(IV)/(PEI/PAA)20 showed the same XRD patterns as the sample of Ce(IV). The absence of characteristic peaks for the PEI/PAA multilayers indicates the disordered and amorphous structure. The Raman spectrum confirmed the coexistence of the cerium dioxide and cerium hydroxide on the sample surface (Figure 6.3b). The strongest band for the Ce-O bonds in CeO$_2$ was expected to be at 465 cm$^{-1}$. However, because of the coexistence with Ce(OH)$_3$, this band was shifted to 452 cm$^{-1}$ in the samples [173]. In addition, there were two weak bands at ~720 cm$^{-1}$ and ~830 cm$^{-1}$ which confirmed the existence of CeO$_2$. The band at 1080 cm$^{-1}$ represented the residual NO$_3^-$ while the band at ~1335 cm$^{-1}$ stood for Mg-OH bond [177,178]. Raman spectra also demonstrated that PAA and PEI formed polymeric multilayers on the cerium compounds. Figure 6.3b shows that there was a strong symmetric COO$^-$ stretching band at 1411 cm$^{-1}$ and a weak asymmetric COO$^-$ stretching band at 1621 cm$^{-1}$ [179,180]. These bands are the essential configuration of the PAA salts [181]. In addition, the band at ~870 and ~901 cm$^{-1}$ represented the C-COO$^-$ stretching. The weak band at 1549 cm$^{-1}$ stood for the NH$_2$ bending which confirmed the existence of PEI [182]. Therefore, the deposition of the cerium conversion layer and the PEI/PAA multilayers on the surface of AZ31 was confirmed using XRD and Raman spectroscopy.

6.3. The corrosion resistance of the PEI/PAA multilayers coating

6.3.1. The EIS results of the PEI/PAA multilayers

Electrochemical impedance spectroscopy (EIS) was used to test the corrosion resistance because of negative difference effect (NDE), where hydrogen evolution continued in the anodic regime of magnesium alloy [183]. When the samples of Ce(IV)/(PEI/PAA)15 and Ce(IV)/(PEI/PAA)20
were exposed to a sodium chloride solution, the PEI/PAA multilayers delaminated from the substrate. However, the sample of Ce(IV)/(PEI/PAA)10 stayed quite stable during the EIS tests. This behavior was probably due to the longer preparation time of Ce(IV)/(PEI/PAA)15 and Ce(IV)/(PEI/PAA)20 during which more cerium compounds were removed by the neutralization reaction with PAA for the sample coated with more than 10 bilayers of PEI/PAA. All the samples including bare AZ31, Ce(III)&Ce(IV), Ce(IV) and Ce(IV)/(PEI/PAA)10 were immersed in a 3.5 wt.% sodium chloride solution for 30 min to obtain a stable open circuit potential before the EIS tests. Figure 6.4a shows the Bode phase results of different samples. The samples of bare AZ31, Ce(III)&Ce(IV) and Ce(IV) demonstrated the same tendency which increased at the intermediate frequencies while decreased to an equivalent value at the low frequencies. There were two time constants in the intermediate frequencies which overlapped but are observed in their corresponding Nyquist plots where the half cycle above zero had two arcs with different radii (Figure 6.4c). On the contrary, the impedance of Ce(IV)/(PEI/PAA)10 kept growing through all the frequency regions and finally achieved ~800 Ω·cm² which was more than 4 times higher than the bare AZ31 sample (Figure 6.4b). This was probably attributed to the buffering effect of the PEI/PAA multilayers which prevented the chloride ions penetration to the substrate [113]. All the samples showed a negative phase at the intermediate frequencies corresponding to the time constants in the Bode impedance plots. This negative phase was due to the conductive property of the coatings on the AZ31 substrate. The samples of bare AZ31, Ce(III)&Ce(IV) and Ce(IV) showed a positive phase at low frequencies. The positive phase is a characteristic behavior of magnesium alloys because of its sensitivity to the corrosive environment. The inductive property was due to the dissolution of magnesium alloy and indicates the initiation of pitting process [21,183]. The sample of Ce(IV)/(PEI/PAA)10 exhibited a negative phase at low frequencies. This behavior confirmed that the buffering effect of the PEI/PAA multilayers which prevented the penetration of the corrosive electrolytes. Figure 6.4c shows the Nyquist plots for different samples. The samples of bare AZ31, Ce(III)&Ce(IV) and Ce(IV) exhibited a negative imaginary impedance at low frequencies which were corresponding to the positive phase in the Bode phase plots. However, the imaginary impedance of Ce(IV)/(PEI/PAA)10 stayed above zero which confirmed the pure conductive property of the multilayer coatings. In addition, the radius of the Nyquist plots of Ce(IV)/(PEI/PAA)10 was bigger than the other samples. These results prove the improved corrosion resistance of Ce(IV)/(PEI/PAA)10.
Figure 6.4 The EIS results of the multilayer coatings. (a) The Bode phase results. (b) The Bode impedance results. (c) The Nyquist plot results.
6.3.2. The buffering effect of the PEI/PAA multilayers

To explore the buffering effect of the PEI/PAA multilayers, the samples of Ce(IV)/(PEI/PAA)5, Ce(IV)/(PEI/PAA)10 and Ce(IV)/(PEI/PAA)20 were prepared for salt immersion tests. A deep cross scratch was made on the surfaces using a scalpel and immersed these samples in a 3.5 wt.% NaCl solution. The corresponding images were taken at 0, 20, 60, 220 and 1360 minutes. Figure 6.5 shows all the images. It was found that black corrosion products formed at the cut of Ce(IV)/(PEI/PAA)20 after 20 min. The corrosion product also generated at the cut of Ce(IV)/(PEI/PAA)10 after 60 min. Finally, the corrosion product formed at the cut of Ce(IV)/(PEI/PAA)5 after 220 min. All the corrosion products concentrated at the cutting interfaces during the 220 min. However, with the increase of immersion time, the PEI/PAA multilayers started to dissolve. Therefore, it was found that a lot of pitting generated on all the surface of Ce(IV)/(PEI/PAA)20. Less pitting formed on the sample of Ce(IV)/(PEI/PAA)10 compared with that of Ce(IV)/(PEI/PAA)20. The sample of Ce(IV)/(PEI/PAA)5 demonstrated the best corrosion resistance. Therefore, the sample with fewer bilayers of PEI/PAA showed a better corrosion resistance. The underlying mechanism was due to the buffering effect of the PEI/PAA multilayers which absorbed the salt ions and the subsequent dissolving of the multilayers. More polyelectrolytes absorbed more salt ions during the same immersion time. As a result, the sample of Ce(IV)/(PEI/PAA)20 absorbed more salt ions than the sample of Ce(IV)/(PEI/PAA)10 and Ce(IV)/(PEI/PAA)5. The absorbed Na⁺ and Cl⁻ ions suppressed the electrostatic attractions between the charged polyelectrolytes of PEI⁺ and PAA⁻ due to the charge screening [128]. Because PEI and PAA are weak polyelectrolytes, the multilayers of PEI and PAA demonstrated an exponential growth [158]. In addition, the cross-link density decreased with the growth of the multilayers due to the extrinsic charge compensation [149,151]. Therefore, the sample with more bilayers of PEI/PAA was more vulnerable to the salt ions.
<table>
<thead>
<tr>
<th>Immersion Time (minutes)</th>
<th>Ce(IV)/(PEI/PAA)$_5$</th>
<th>Ce(IV)/(PEI/PAA)$_{10}$</th>
<th>Ce(IV)/(PEI/PAA)$_{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>20</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>60</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
<tr>
<td>220</td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
<tr>
<td>1360</td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 6.5 The salt immersion tests of the multilayer coatings
Figure 6.6 The cross-section images of the cerium conversion layer of the multilayer coatings. (a) Ce(IV)/(PEI/PAA)5. (b) Ce(IV)/(PEI/PAA)10. (c) Ce(IV)/(PEI/PAA)15. (d) Ce(IV)/(PEI/PAA)20.

In addition to the buffering effect of the PEI/PAA multilayers, the cerium conversion layer also played a significant role in the corrosion resistance. The samples of Ce(IV)/(PEI/PAA)5, Ce(IV)/(PEI/PAA)10, Ce(IV)/(PEI/PAA)15 and Ce(IV)/(PEI/PAA)20 were mounted using the hot mounting machine. The PEI/PAA multilayers melted during the high pressure and temperature mounting environment. Then, the mount was broken and the cross-sections of the samples were observed. Figure 6.6 shows that the thickness was 1.25, 1.19, 1.01 and 0.728 microns for the samples of Ce(IV)/(PEI/PAA)5, Ce(IV)/(PEI/PAA)10, Ce(IV)/(PEI/PAA)15 and Ce(IV)/(PEI/PAA)20 respectively. The decrease of thickness with the increase of multilayers of PEI/PAA confirmed the reaction between the polyelectrolytes and the cerium compounds during the coating preparation process. Because the cerium conversion layer also contributed to the corrosion resistance of magnesium alloy, the thicker layer provided a better protection the
magnesium substrate. This result agreed with the observation in the salt immersion tests for different samples.

6.4. The self-healing behavior and mechanism of the PEI/PAA multilayers

6.4.1. The self-healing behavior of the PEI/PAA multilayers

![Image](image_url)

Figure 6.7 The limited self-healing behavior of the sample of Ce(IV)/(PEI/PAA)5. (a) Before immersion in water for 10 min. (b) After immersion in water for 10 min.

One of the most significant properties of advanced anticorrosion coatings is self-healing. To explore the self-healing ability of the polymeric coating, a scalpel was used to cut on the sample of Ce(IV)/(PEI/PAA)5, Ce(IV)/(PEI/PAA)10 and Ce(IV)/(PEI/PAA)20. After that, a droplet of water was dropped on the surface and dried the surface after 10 or 20 min with the lab wipers and dust remover. The samples were fixed under the microscope with tapes to ensure the in-situ observation before and after healing. Because the scratches were made manually, the width of scratches ranged from 10 to 22 microns. It was found that the sample of Ce(IV)/(PEI/PAA)5 demonstrated a limited self-healing ability. A cut was made on the surface of Ce(IV)/(PEI/PAA)5. Figure 6.7 shows that the cut was still visible on the surface after 10 min (Figure 6.7). Figure 6.8a shows that the cuts with a width of ~10 microns were made on the surface of Ce(IV)/(PEI/PAA)10. After cutting, a droplet of water was dropped on the sample surface and leave the sample under ambient environment without heating or light illumination. The surface was dried after a healing
time of 10 minutes. Figure 6.8b shows the cut mended and most of the original morphology of the coating recovered.

Figure 6.8 The self-healing behavior of the multilayer coatings. (a) The cut with a 10-microns cut on the sample of Ce(IV)/(PEI/PAA)10. (b) The sample of Ce(IV)/(PEI/PAA)10 after immersion in water for 10 min. (c) The cut with an 11-microns cut on the sample of Ce(IV)/(PEI/PAA)10. (d) The sample of Ce(IV)/(PEI/PAA)10 after immersion in water for 20 min. (e) The cut with a 20-microns cut on the sample of Ce(IV)/(PEI/PAA)20. (f) The sample of Ce(IV)/(PEI/PAA)20 after immersion in water for 10 min. (g) The cut with a 22-microns cut on the sample of Ce(IV)/(PEI/PAA)20. (h) The sample of Ce(IV)/(PEI/PAA)20 after immersion in water for 20 min.
However, a little mark was still observed on the surface. The process was repeated on the same sample for a second time with a longer healing time of 20 minutes (Figure 6.8c). Figure 6.8d shows that the cut healed after 20 min recovered better than the sample healed after 10 minutes. The cut mark was only viewed after magnification of the image. The same tests were applied to the sample of Ce(IV)/(PEI/PAA)20. Figure 6.8e and f show that the cut with a width of ~22 microns was mostly healed after a healing time of 10 minutes. Furthermore, the sample of Ce(IV)/(PEI/PAA)20 completely recovered from the cut with a width of ~22 microns after a healing time of 20 minutes (Figure 6.8g and h). These results are similar to the results of 30 bilayers of PEI/PAA prepared on slide glasses [69,184]. The healing time of 10 min was much faster than the 48 hours required for the healing with the agent incorporated in the self-healing coatings [185,186]. This healing ability was also more rapid than for the PEI/PAA system prepared on aluminum which requires 12 hours to heal the scratch partially [114]. The excellent performance of the coating was attributed to the tuning of pH values. The pH values of PEI and PAA were tuned to be 9.5 and 4.5, respectively. Compared with the pH values of 9 and 5.5 used in other work, the PEI/PAA system was expected to have a lower number of crosslinks of electrostatic interactions. This allowed a higher molecular mobility which contributed to faster self-healing of the multilayers coating. It was found that the self-healing ability of this coating was time- and thickness-dependent. In addition, it was regarded as an autonomous intrinsic self-healing coating which healed the damage without any energy input.

6.4.2. The self-healing mechanism of the PEI/PAA multilayers

As the self-healing process took place in the presence of water, it was the swelling behavior of this coating that brought the separated parts together. Therefore, the samples having different numbers of bilayers were immersed in the deionized water. The weight of water uptake per square meter was measured after different swelling times. Figure 6.9a. shows that the sample of Ce(IV)/(PEI/PAA)10 absorbed ~18 g/m² after the swelling time of 5 minutes, while the sample of Ce(IV)/(PEI/PAA)20 absorbed ~36 g/m². More bilayers of PEI/PAA absorbed more water during the same swelling time. This result is coincident with the better self-healing ability of Ce(IV)/(PEI/PAA)20 comparing with Ce(IV)/(PEI/PAA)10. Furthermore, all the samples absorbed more than 40% of water during the first 10 min. The absorbing rate decreased with the increase of swelling time. Especially, the sample of Ce(IV)/(PEI/PAA)10 absorbed more than 75%
of water during the first 10 min and saturated after 10 min. This result agreed with the time of 10 min that was required to heal the scratch on the sample surface. Figure 6.9b shows that the swelling ratio increased with the swelling time and the number of multilayers. The swelling ratio was defined as the ratio of the weight of water uptake to the weight of dry coatings [29,35]. The swelling ratio increased to ~2.5 during the first 10 minutes while slowed down afterward. With a swelling time of 1200 minutes, the swelling ratio increases from 4.3 of Ce(IV)/(PEI/PAA)10 to 6.8 of Ce(IV)/(PEI/PAA)20. This result explains the self-healing behavior of the samples which took 10 minutes to heal the scratch. The self-healing ability was much faster than the same PEI/PAA multilayers prepared on aluminum alloys which took 12 hours to partially heal the scratch in the presence of salt water [179]. The swelling ratio increased with the decrease of crosslink density [29] and the smaller crosslink density led to a higher mobility of the molecular chains which favored the self-healing ability. The better self-healing ability of the samples was attributed to the lower crosslink density and the better molecular chain mobility because the pH values of PEI and PAA in their work were tuned to 9 and 5.5, respectively. In addition, the sample with 20 bilayers of PEI/PAA demonstrated a better self-healing ability while the sample with 5 bilayers only showed a limited self-healing ability (Figure 6.7). Both PEI and PAA are weak polyelectrolytes which showed an exponential growth due to the “in-and-out” mechanism [153]. The thickness of 5 to 20 bilayers of PEI/PAA increased from ~50 nanometers to ~15 micrometers [184,187]. Therefore, more bilayers of PEI/PAA led to a higher swelling ratio and better chain mobility. In addition, lower amounts of PEI/PAA were deposited on the surface for the first 5 bilayers. As a result, a thinner coating required a higher swelling ratio to heal the scratch with the same size. However, the swelling ratio decreased when the layer was thinner. Therefore, the 5 bilayers cannot provide a sufficient self-healing ability to heal the scratch. With the exponential growth of film thickness, more amounts of PEI/PAA were deposited on the surface which induced the better self-healing ability. Therefore, the multilayer coatings were expected to have a better healing ability with the increase of the number of bilayers.
Figure 6.9 The swelling behavior of the multilayer coatings. (a) The water uptake. (b) The swelling ratio.

Compared with the linear growth polyelectrolytes, the exponential growth behavior of PEI/PAA multilayers induced a looser cross-linking at the surface and thus a better chain mobility for the coatings with more layers allowing the inter-diffusion of polyelectrolytes across the scratch [188]. The hardness of the samples was tested to confirm that the cross-link density also contributed to the chain mobility. To make a comparison, the control samples of PEI and PAA with a pH value of 7 were prepared. As a result, the PEI and PAA at this pH value were stronger charged and expected to demonstrate a higher cross-link density. The control sample was denoted as Ce(IV)/(PEI7/PAA7)10. The hardness of the samples was measured and four different points on the samples were recoded. The force was set to be 300gf for all the tests. Figure 6.10 shows that the hardness of Ce(IV)/(PEI7/PAA7)10 was ~65HV which was similar to that of Ce(III)&Ce(IV) and Ce(IV). In addition, the hardness stayed stable after immersion in water.
for 10 min. This result was attributed to the high cross-link density of Ce(IV)/(PEI7/PAA7)10 which induced a higher stiffness and limited the chain mobility. However, the sample of Ce(IV)/(PEI/PAA)10 demonstrated a much lower hardness ~45 HV. The hardness further decreased to ~40 HV after immersion in water for 10 min. Water played as a plasticizer in the PEI/PAA multilayers and softened the molecular chains [184]. As a result, the sample of Ce(IV)/(PEI/PAA)10 after water immersion possessed a higher chain mobility which contributed to the self-healing ability.

![Figure 6.10 The Vickers hardness of the multilayer coatings.](image)

**6.5. Summary**

In Chapter 6, the cerium conversion layer on the magnesium alloy was prepared by immersing the sample in a 0.05 M cerium nitrate solution for 30 min and followed by sintering at 80 degrees Celsius for 30 min. There formed a continuous cerium conversion layer with minor cracks which
provided a good binding to the following multilayers of polyelectrolytes. The multilayers of polyelectrolytes consisted of poly(ethylene mine) (PEI) and poly(acrylic acid) (PAA). It was the electrostatic attractions that bound the positively charged PEI and negatively charged PAA on the surface.

This multilayer coating exhibited an improved corrosion resistance compared with the bare AZ31 and the sample coated with cerium conversion layer. This improved corrosion resistance was attributed to the buffering effect of the PEI/PAA multilayers which suppressed the attack from the chloride ions. The corrosion resistance decreased with the increase of bilayers of PEI/PAA. In addition, this multilayer coating with more than 10 bilayers of PEI/PAA exhibited an excellent intrinsic self-healing ability in the presence of water.

In summary, it was found that the sample of Ce(IV)/(PEI/PAA)10 reached a compromise of an excellent corrosion resistance with a rapid self-healing ability.
CHAPTER 7

THE GRAPHENE OXIDE (GO) INCORPORATED PEI/PAA MULTILAYERS SELF-HEALING COATING ON MAGNESIUM ALLOY AZ31

7.1. Overview

Chapter 7 focused on the role of graphene oxide (GO) in self-healing and corrosion resistance of the multilayer coating. The graphene oxide (GO) was added to the poly(ethylene imine)/poly(acrylic acid) (PEI)/(PAA) multilayers. GO has been applied in the system due to its ultrahigh mechanical strength and potential application in corrosion resistance. Because of the high aspect ratio and barrier property of GO, it has been studied as the corrosion inhibitors.

The morphology of GO and the GO incorporated multilayers was observed using SEM. The XRD patterns and Raman spectra confirmed the deposition of GO in the multilayer coating. Thermogravimetric analysis and differential scanning calorimetry were used to study the thermodynamic property of the multilayers.

The self-healing behavior of the GO incorporated multilayers was tested. The self-healing ability was comparable to the multilayers without GO. The hardness result confirmed that the high flexibility of the PEI/PAA multilayers contributed to the self-healing ability.
Finally, the long period protection ability of the multilayers was tested with and without GO. The EIS results demonstrated that the multilayers with GO provided a better corrosion resistance to the magnesium substrate compared with that without GO. The feature of GO in the corrosion resistance was further analyzed using SEM, EDS, XRD and Raman spectroscopy. The degradation mechanisms of the coating with and without GO were discussed. Part of the results of this chapter has been published in “F. Fan, C.Y. Zhou, X. Wang, J. Szpunar, Layer-by-Layer assembly of a self-healing anticorrosion coating on magnesium alloys. ACS Applied Materials & Interfaces, 7 (2015), 27271 – 27278”. All the experiments were designed and conducted by Fan Fan. The manuscript was written by Fan Fan. The graphene oxide was prepared by Chunyu Zhou. The manuscript was reviewed and corrected by Xu Wang and Jerzy Szpunar. The Copyright and permission for reusing the context, figures, and tables of these published results have been attached in the appendix.

7.2. Preparation and characterization of the multilayer coating

7.2.1. Preparation of the multilayer coating

The sample was immersed in the 0.05 M cerium nitrate solution for 30 min and sintered at 80 degrees Celsius for 30 min to obtain the cerium conversion layer. Before the deposition of PEI/PAA multilayers, the cerium-based conversion layer coated sample was immersed in the PEI solution and the 0.1 M graphene oxide solution to obtain Ce(IV)/PEI/GO. Therefore, the positively charged PEI bound with the negatively charged GO via the electrostatic attractions [189,190].

The sample of Ce(IV)/PEI/GO was then alternatively dipped in positively charged PEI, deionized water, negatively charged PAA and deionized water. The deposition of a LbL assembly of PEI/PAA multilayers was repeated 10 times to obtain the final product of Ce(IV)/PEI/GO/(PEI/PAA)10. To compare the effect of graphene oxide, samples of Ce(IV)/(PEI/PAA)10 without graphene oxide were also prepared. Figure 7.1 shows the process details of the sample preparation.
SEM was used to analyze the morphology of the graphene oxide sheet and the graphene oxide coated sample. Figure 7.2a shows the morphology of the graphene oxide and confirmed the high aspect ratio. The high aspect ratio of the graphene oxide provided the possibility for a good corrosion protection because of the torturous pathway formed to retard the penetration of the corrosive electrolyte [191]. When preparing the multilayer coating with graphene oxide, graphene oxide was added between the cerium-based conversion layer and the PEI/PAA multilayers. Figure 7.2b confirms the uniform distribution of graphene oxide on the sample surface. This layer played a major role in self-healing and especially in corrosion resistance.
Characterization of the multilayer coating

X-ray diffraction (XRD) and Raman spectroscopy were used to identify the compositions of the coatings. Both the samples of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 showed a peak at 2-theta of 43.1 degrees which indicated the deposition of CeO2 on the sample surface (Figure 7.3a). Because the amorphous structure of PEI and PAA these structures cannot be identified by XRD, the XRD patterns of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10
Figure 7.3 The XRD patterns and Raman spectra of the multilayer coating with and without GO. (a) XRD pattern. (b) Raman spectra.
are the same. Raman spectroscopy was used to identify the deposition of GO and polymer on the surface. Figure 7.3b shows a peak at 453 cm$^{-1}$ of the Raman spectrum of Ce(IV)/(PEI/PAA)10 which was broadened and shifted from the standard peak of cerium oxide at 465 cm$^{-1}$. This was probably due to the coexistence of Ce(III) and Ce(IV) [173]. The peak at 1046 cm$^{-1}$ indicated the presence of residual NO3$^-$ ions which promoted passivating the sample surface [173,177]. The peaks representing the stretching of C-COO$^-$ and the symmetric stretching of COO$^-$ were shown at 902 cm$^{-1}$ and 1416 cm$^{-1}$ on the spectrum of Ce(IV)/(PEI/PAA)10, respectively [181]. The COO-bond originated from the ionization of the carboxylic acid groups (COOH) of PAA was responsible for the absence of characteristic carbonyl bonds (C=O) at around 1700 cm$^{-1}$. These results confirmed the successful deposition of PAA on the surface. The peak of symmetric NH3$^+$ deformation at 1527 cm$^{-1}$ illustrated the deposition of PEI on the surface [182]. The CH2 wagging and CH2 bending from the molecular chains of PEI and PAA generated the peaks at 1315 and 1456 cm$^{-1}$ [182]. For the sample of GO, two peaks were shown at 1357 and 1593 cm$^{-1}$ which represented the G band and D band, respectively. The G band is caused by the in-plane vibration of hybridized sp$^2$ carbon while the D band is due to the induced structural defects and disorder of GO [192]. Figure 7.3b shows that the D band and G band of Ce(IV)/PEI/GO/(PEI/PAA)10 shifted respectively to 1344 cm$^{-1}$ and 1596 cm$^{-1}$. The opposite shifting resulted from the disordered distribution of GO sheets that was induced by the deposition process [193]. The sample of Ce(IV)/PEI/GO/(PEI/PAA)10 had two additional peaks at 1400 and 1645 cm$^{-1}$. These peaks resulted from the O-H vibration of C-OH group and the stretching of symmetric C=O dimer of the functional groups of GO [163,194]. Furthermore, the peak of cerium ions shifted to 460 cm$^{-1}$ in the sample of Ce(IV)/PEI/GO/(PEI/PAA)10. This was probably due to the reaction between GO and the residual cerium hydroxide during the deposition.

In addition to the chemical structure analysis, the thermodynamic properties of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 were studied. The coatings of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 were carefully removed for TGA and DSC tests. The TGA and DSC were conducted in a nitrogen atmosphere with a heating rate of 20°C/min from room temperature to 1000°C using the SDT Q600 from TA instrument. The starting weight of the coatings with and without GO was 1.85 and 1.95 mg, respectively. Figure 7.4a shows that the weight percentage of the coating without GO decreased continuously before 400 °C. This was due to the evaporation of water molecules at ~100°C and the dehydration reaction between
carboxyl groups and amine groups at ~200°C [179,195]. When the temperature increased to 400 °C, the weight percentage dropped fast from ~60% to ~20%. The heat flow plot also shows a corresponding exothermic peak at this region which indicated the decomposition of PEI/PAA [196]. When the temperature kept increasing, the weight percentage decreased continuously to zero at 800 °C. The PEI/PAA multilayers were further pyrolyzed to carbonaceous materials [197].

Regarding the sample of Ce(IV)/PEI/GO/(PEI/PAA)10, the oxygen containing groups of GO were removed at ~200°C (Figure 7.4b) [198]. An additional strong exothermic peak and a second weight drop were observed between 500 and 600 °C. This might be attributed to the decomposition of GO to graphite-like materials [199,200]. Finally, the sample of Ce(IV)/PEI/GO/(PEI/PAA)10 left around 5 wt.% at 1000 °C. Because the char yield is close to the GO content, the GO loading percentage was estimated to be ~5 wt.% [199].

Figure 7.4 The TGA and DSC results of the sample of (a) Ce(IV)/(PEI/PAA)10 and (b) Ce(IV)/PEI/GO/(PEI/PAA)10.
7.3. The self-healing behavior of the multilayer coating

The self-healing ability of Ce(IV)/PEI/GO/(PEI/PAA)10 in the presence of water was tested to compare with Ce(IV)/(PEI/PAA)10 and Ce(IV)/(PEI/PAA)20. A cut on the surface was made using a scalpel. Figure 7.5 shows the cut made on the sample and the surface healed after 10 min in the presence of water. It was observed that the self-healing ability of Ce(IV)/PEI/GO/(PEI/PAA)10 was better than that of Ce(IV)/(PEI/PAA)10 because the cut totally healed after 10 min. This ability was equivalent to that of Ce(IV)/(PEI/PAA)20. This result indicates that the hydrogen bonding induced by GO was the main factor promoting the self-healing behavior of the polyelectrolytes [35,50].

![Figure 7.5](image)

Figure 7.5 The self-healing behavior of the sample of Ce(IV)/PEI/GO/(PEI/PAA)10.

Because the flexibility of molecular chains is also critical to the self-healing ability, the hardness of the sample of Ce(IV)/I/GO/(PEI/PAA)10 was measured to compare with that of Ce(IV)/(PEI/PAA)10. Four different points on the samples were recorded. The force was set to be 300gf for all the tests. Figure 7.6 shows that the dry sample of Ce(IV)/PEI/GO/(PEI/PAA)10 demonstrated a relatively high hardness of ~63 HV which was comparable to that of Ce(IV). This improvement of hardness was attributed to the excellent mechanical strength of GO [201]. However, with the immersion of water, the hardness of Ce(IV)/PEI/GO/(PEI/PAA)10 dropped to ~37 HV which was lower than that of Ce(IV)/(PEI/PAA)10 after water immersion. This reduction was probably due to the less attraction between the GO layer and the PEI/PAA multilayers.
compared with the attraction between the cerium conversion layer and the PEI/PAA multilayers. The reduced constraint provided more flexibility to the PEI/PAA multilayers and induced a better self-healing ability.

![Graph showing Vickers hardness comparison](image)

Figure 7.6 Comparison of the Vickers hardness for the samples of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 before and after immersion.

### 7.4. The corrosion resistance of the multilayer coating

#### 7.4.1. The EIS results of the multilayer coating

Electrochemical impedance spectroscopy (EIS) was used to test the corrosion resistance of all samples. Figure 7.7 to 7.9 respectively shows the Bode phases, the Bode impedance and the Nyquist plots of the samples of bare AZ31, Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 after immersion in a 3.5 wt.% NaCl solution for 0.5, 2, 4, 24, 48
and 72 hours. For the Bode phase results, an ideal coating was expected to exhibit a phase of -90° due to its pure capacitive property [202]. However, because of the existence of porosity in the coatings and penetration of electrolytes, the real coating demonstrated a Bode phase which was larger than -90°. Figure 7.7a shows that after 0.5 h immersion, all the samples including bare AZ31, Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 demonstrated a capacitive response with a Bode phase around -70° at the intermediate frequencies (10 – 10k Hz). The capacitive responses of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 were observed for the multilayer coatings; while the capacitive response of bare AZ31 was due to the corrosion products formed on the surface. In addition, the Bode phase of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 showed another capacitive behavior at the low frequencies (10m – 10 Hz). This behavior was attributed to the charge transfer that controlled the reaction at the metal/coating interfaces. However, the sample of AZ31 demonstrated an inductive behavior in the low-frequency region. The decreased impedance of bare AZ31 at low frequencies in the Bode impedance plot agreed with the inductive behavior (Figure 7.8a). This was commonly observed in magnesium samples and was probably due to the formation of corrosion pits [21]. At the same time, the Bode impedance of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 had a higher value compared with that of bare AZ31 (Figure 7.8a). Because the impedance value at the lowest frequency indicated the corrosion resistance of the sample, the coated samples showed a better anticorrosion ability than bare AZ31. The larger radii of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 in the Nyquist plots also confirmed their better corrosion resistance (Figure 7.9a). After immersion of 2 h, the phase angles of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 decreased to -80° while the capacitive peaks of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 shifted to a lower frequency (Figure 7.7b). These results indicate the improved corrosion resistance of the multilayer coatings. The improvement resulted from the precipitation of corrosion products which decreased the permeability of the coatings [203,204]. Both the Bode impedance and Nyquist plots show the increase of the corrosion resistance of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 (Figure 7.8b and 7.9b). After immersion of 4 h, the capacitive behavior at low frequencies of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 transferred to an inductive behavior while the phase shift of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 increased to -70° (Figure 7.7c). These results indicate the degradation of the coatings. The reduced impedance of
Bode plots and the decreased radii of Nyquist plots illustrated that the corrosion resistance of the coatings decreased (Figure 7.8c and 7.9c). After immersion of 24 h, the inductive phase at the low frequencies of bare AZ31 increased to more than 20° (Figure 7.7d). This behavior demonstrated a further degradation of the bare AZ31 samples. Figure 7.8d shows that the impedance of Ce(IV)/PEI/GO/(PEI/PAA)10 decreased to the same level as that of Ce(IV)/(PEI/PAA)10. Meanwhile, the Nyquist plots of Ce(IV)/PEI/GO/(PEI/PAA)10 overlapped with that of Ce(IV)/(PEI/PAA)10 (Figure 7.9d). All the results demonstrated a small reduction of the corrosion resistance of Ce(IV)/PEI/GO/(PEI/PAA)10. However, the corrosion resistance of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 were still higher than that of bare AZ31. After immersion of 48 h, the inductive phase of Ce(IV)/PEI/GO/(PEI/PAA)10 shifted to a higher frequency (Figure 7.7e). This behavior accompanied by the decrease of corrosion resistance was shown in the Bode impedance and Nyquist plots (Figure 7.8e and 7.9e). After immersion for 72 h, bare AZ31 exhibited a high diffusion process as the Bode phase increased fast at the high-frequency region which corresponded to the drop of Bode impedance at the high-frequency region (Figure 7.7f and 7.8f). The sample of Ce(IV)/(PEI/PAA)10 degraded further as the capacitive peak showed a higher frequency compared with the sample of bare AZ31 and Ce(IV)/PEI/GO/(PEI/PAA)10. Figure 7.8f demonstrates that the impedance of Ce(IV)/(PEI/PAA)10 dropped to the same level as the bare AZ31. This indicates the loss of corrosion protection of the multilayer coating without GO. However, the sample of Ce(IV)/PEI/GO/(PEI/PAA)10 demonstrated a comparatively higher impedance. In addition, the Nyquist plots show that the sample of Ce(IV)/PEI/GO/(PEI/PAA)10 had a better corrosion resistance compared with the sample of Ce(IV)/(PEI/PAA)10 (Figure 7.9f). This difference in corrosion behaviors originated from the strong barrier property GO against the electrolyte penetration [136].
Figure 7.7 The EIS results of Bode phases at (a) 0.5 h, (b) 2 h, (c) 4 h, (d) 24 h, (e) 48 h and (f) 72 h.
Figure 7.8 The EIS results of Bode impedances at (a) 0.5 h, (b) 2 h, (c) 4 h, (d) 24 h, (e) 48 h and (f) 72 h.
To quantify the corrosion resistance of different samples after different immersion times, the EIS results were fitted with the 4 equivalent circuits shown in Figure 7.10. Mode 1 was proposed by Bland et al. [205] to analyze the corrosion resistance of AZ31 (Figure 7.10a). This model properly...
fitted the data of bare AZ31 from 0.5 to 48 h. However, because of the appearance of a strong diffusion process, another series of resistor and inductor were added to the circuit to fit the data of bare AZ31 at 72 h (Figure 7.10b). For model 1 and model 2, the time constant of $R_1 & C_1$ represents the outer loose layer while the time constant of $R_2 C_2$ can be attributed to the inner barrier layer of corrosion products mainly because magnesium rapidly formed a oxide/hydroxide layer when exposed to corrosive electrolytes [206]. Because of the absence of inductive behavior, mode 3 was employed to fit the data of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 at 0.5 and 2 h (Figure 7.10c). After the appearance of inductive phases, model 4 with an additional series of resistor and inductor was applied to fit the data of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 from 4 to 72 h (Figure 7.10d). For the coated samples, the time constants of $R_1 C_1$ and $R_2 C_2$ corresponded to the multilayer coatings while the constant of $R_5 C_3$ was derived from the capacitive behavior at the metal/coating interfaces [202]. In addition, the inductors $L_1$ and $L_2$ in all models represent the inductive behavior at the metal/coating interfaces. All the fitted data were shown in Table 7.1. The capacitance value of $C_1$ of different samples increased with time. The capacitance value equals to $\frac{\varepsilon_r \varepsilon_o A}{4\pi d}$, where $\varepsilon_r$ is the dielectric constant, $\varepsilon_o = 1$ is the vacuum permittivity, $A$ is the coating areas and $d$ is the thickness of coatings [206]. Therefore, the increased capacitance could be attributed to the absorption of water and/or dissolving of the multilayer coatings.

![Figure 7.10 The equivalent circuits of the EIS results.](image)
<table>
<thead>
<tr>
<th>Sample</th>
<th>Time</th>
<th>C (Ω·cm²)</th>
<th>Rs (Ω·cm²)</th>
<th>Rs (Ω·cm²)</th>
<th>Rs (Ω·cm²)</th>
<th>Rs (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>10.01</td>
<td>3.74E-5</td>
<td>1027</td>
<td>1027</td>
<td>1027</td>
<td>1027</td>
</tr>
<tr>
<td>1</td>
<td>12.70</td>
<td>1.56E-5</td>
<td>1045</td>
<td>1045</td>
<td>1045</td>
<td>1045</td>
</tr>
<tr>
<td>2</td>
<td>10.45</td>
<td>1.56E-5</td>
<td>1045</td>
<td>1045</td>
<td>1045</td>
<td>1045</td>
</tr>
</tbody>
</table>

**Table 7.1 Fitted EIS data for bare AZ31, Ce(IV)/GO/PEI/PAA10 and Ce(IV)/GO/PEI/PAA10**
7.4.2. The polarization resistance and protection efficiency of the multilayer coating

(a)

(b)

Figure 7.11 The polarization resistance and protection efficiency as a function of time. (a) The polarization resistance. (b) The protection efficiency.
Because different models were applied to fit the data of different samples, the corrosion resistance cannot be compared directly. Instead, the polarization resistance was calculated to compare the corrosion resistance of different samples. Polarization resistance was defined as the difference between the impedance when frequency equaled to zero and the solution resistance [183]. According to this definition, the polarization resistance was calculated using equations as follows:

model 1: \[
\frac{1}{R_p} = \frac{1}{R_1 + R_2} + \frac{1}{R_3}
\] \hspace{1cm} (7.1)

model 2: \[
\frac{1}{R_p} = \frac{1}{R_1 + R_2} + \frac{1}{R_3} + \frac{1}{R_4}
\] \hspace{1cm} (7.2)

model 3: \[
\frac{1}{R_p} = \frac{1}{R_1 + R_2 + R_5}
\] \hspace{1cm} (7.3)

model 4: \[
\frac{1}{R_p} = \frac{1}{R_1 + R_2 + R_5} + \frac{1}{R_3}
\] \hspace{1cm} (7.4)

Figure 7.11a shows that the polarization resistance of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 were 2 orders higher than that of bare AZ31 at 0.5 and 2 h. The polarization resistance of Ce(IV)/(PEI/PAA)10 started to decrease after immersion of 4 h and stayed stable from 4 to 48 h. It finally dropped to the same order as bare AZ31 after 72 h. Meanwhile, the polarization resistance of Ce(IV)/PEI/GO/(PEI/PAA)10 decreased slowly but retained an order’s higher polarization resistance compared with bare AZ31 from 4 to 72 h. The protection efficiency \(P_{EF}\%\) of the multilayer coatings was calculated using the following equation [207]:

\[
P_{EF}\% = \frac{R_p^{-1}(\text{uncoated}) - R_p^{-1}(\text{coated})}{R_p^{-1}(\text{uncoated})} \times 100\%
\] \hspace{1cm} (7.5)

where \(R_p^{-1}(\text{uncoated})\) is the polarization resistance of bare AZ31 and \(R_p^{-1}(\text{coated})\) represents the polarization resistance of Ce(IV)/(PEI/PAA)10 or Ce(IV)/PEI/PAA/(PEI/PAA)10. The protection efficiencies of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/PAA/(PEI/PAA)10 at different immersion times were calculated. Figure 7.11b shows that the \(P_{EF}\%\) of Ce(IV)/(PEI/PAA)10 decreased from ~95% to ~70% from 4 to 48 h and dropped to ~40% after 72 h. This result illustrates that the PEI/PAA multilayers provided a good corrosion protection during the first 48 h.
but almost lost the protection after 72 h. The $P_{EF} \%$ of Ce(IV)PEI/GO/(PEI/PAA)10 kept decreasing from 4 to 48 h due to the degradation of the multilayer coating. However, the degrading speed was slower than that of Ce(IV)/(PEI/PAA)10. Therefore, the $P_{EF} \%$ Ce(IV)/PEI/PAA/(PEI/PAA)10 was always higher than that of Ce(IV)/(PEI/PAA)10. It finally increased to a relatively high value of $\sim 85\%$ after the immersion of 72 h. This result was due to the failure of the corrosion protection of bare AZ31 after immersion of 72 h. The long period protection and slow degradation of the GO incorporated multilayer coating confirmed that GO further improved the corrosion resistance.

7.5. The degradation process and protection mechanism of the multilayer coating

7.5.1. The degradation process of the multilayer coating

Because the corrosion resistance of Ce(IV)/(PEI/PAA)10 dropped much faster than that of Ce(IV)/PEI/GO/(PEI/PAA)10 after immersion of 72 h, exploring the different degrading mechanisms of these two coatings were critical for explaining their behavior. Figure 7.12 and 7.13 show the surface morphology and chemical distribution of Ce(IV)/(PEI/PAA)10 and Ce(IV)/PEI/GO/(PEI/PAA)10 after 72 h immersion. The optical images of the samples were shown on the left. The green area was covered by tapes during the EIS tests and regarded as an intact spot (spot 3, green). Both the samples exposed a surface with an area of 1 cm$^2$ to the 3.5 wt.% NaCl solution. The exposed area was classified into a lightly corroded area (spot 2, yellow) and a heavily corroded area (spot 1, red). The differences in surface morphology of these regions were observed using SEM. The SEM images of different spots of different samples were shown in the middle. The areas highlighted by the red, yellow and green color on the SEM images were scanned using EDS. All the EDS results were shown on the right. Figure 7.12 illustrates that spot 3 on the sample of Ce(IV)/(PEI/PAA)10 had a similar structure to the PEI/PAA multilayers before immersion. The EDS result of spot 3 revealed only 1.1% chloride ions. This proves that the area under the tape was not heavily corroded by NaCl. The relatively high content of carbon and nitrogen confirmed the existence of PEI/PAA multilayers because carbon and nitrogen were mainly in the polyelectrolyte multilayers. The SEM image of spot 2 on Ce(IV)/(PEI/PAA)10
demonstrates the same morphology as the cerium based conversion layer. The EDS results show that the amount of carbon and nitrogen decreased from spot 3 to spot 2. This result indicates the decomposition of the polyelectrolyte multilayers. In addition, the increased amount of cerium atoms confirmed the exposure of the cerium based conversion layer. The SEM image of spot 3 reveals the formation of corrosion products and big cracks on the surface of Ce(IV)/PEI/PAA/(PEI/PAA)10. The EDS results of this area show that oxygen and magnesium dominated with an amount of 56.8% and 31.7%, respectively. This result proves the formation of corrosion products which was probably magnesium hydroxide and/or magnesium oxide.

Figure 7.12 The surface morphology and chemical distribution of the sample of Ce(IV)/(PEI/PAA)10.
The sample of Ce(IV)/PEI/GO/(PEI/PAA)10 after 72 h immersion was also analyzed and characterized using SEM and EDS. Figure 7.13 shows that spot 3 of Ce(IV)/PEI/GO/(PEI/PAA)10 had the same morphology as the sample of Ce(IV)/PEI/GO/(PEI/PAA)10 before immersion. The high content of carbon and nitrogen confirmed the existence of GO incorporated PEI/PAA multilayers. The SEM image of spot 2 shows that part of the area exposed a morphology similar to the cerium based conversion layer. The EDS result confirmed the absence of cerium which had an atomic ratio of 1.2%. In addition, the cerium map shows the distribution of cerium which agreed with the morphology on the SEM image. Compared with the total exposure of the cerium conversion layer on spot 2 of Ce(IV)/PEI/PAA)10, the partial exposure of the cerium conversion layer on spot 2 of Ce(IV)/PEI/GO/(PEI/PAA)10 indicates that the incorporation of GO in the
PEI/PAA multilayers improved the protection property. The SEM image shows that spot 3 of Ce(IV)/PEI/GO/(PEI/PAA)10 was also heavily corroded. The EDS result confirmed that this area was also covered by the corrosion products of magnesium and oxygen. However, the surface had a solid morphology without cracks. This structure provided a better protection to the underlying non-corroded magnesium compared with the cracked surface. The results of the surface morphology and chemical distribution accounted for the better corrosion resistance of Ce(IV)/PEI/GO/(PEI/PAA)10 observed in the EIS results.

To analyze the corrosion products, the sample of bare AZ31 after 72 h immersion at different spots on Ce(IV)/(PEI/PAA)10 specimen was characterized using XRD and Raman spectroscopy (Figure 7.14). Figure 7.14a shows that the XRD pattern of bare AZ31 had four additional peaks at 27.9°, 58.1°, 79.3° and 93.6° representing magnesium hydroxide. All the four peaks were also observed on spot 1 and spot 2 of both Ce(IV)/(PEI/PAA)10 (Figure 7.14a). These results confirmed that the corrosion product was magnesium hydroxide. However, these peaks cannot be observed on spot 3 of Ce(IV)/(PEI/PAA)10. This result confirmed that the area of spot 3 is not corroded by the salt ions. Two more peaks representing magnesium nitrate were identified on spot 1 and spot 2 of Ce(IV)/(PEI/PAA)10 (Figure 7.14a). This was probably due to the reaction of nitric acid in PEI with magnesium hydroxide and the formation of magnesium nitrate during the deposition process. The peak representing cerium oxide at 43.2 on both spot 2 and spot 3 was observed. This result agreed with the observation of SEM and EDS. However, the absence of the peak of cerium oxide on spot 1 of Ce(IV)/(PEI/PAA)10 confirmed the dissolution of cerium oxide during the EIS tests.

Figure 7.14b shows that there were three peaks representing magnesium hydroxide at 252, 432 and 1088 cm⁻¹ on the Raman spectrum of bare AZ31. Because the standard peak of cerium oxide is at 465 cm⁻¹, the peak at 453 cm⁻¹ of spot 3 on Ce(IV)/(PEI/PAA)10 was a combined peak of cerium oxide (465 cm⁻¹) with magnesium hydroxide (432 cm⁻¹). The peak at 1083 cm⁻¹ indicates the formation of magnesium hydroxide during the deposition process. The XRD patterns of spot 1 and spot 2 on Ce(IV)/(PEI/PAA)10 demonstrate that the combined peak shifted to 435 cm⁻¹. This result confirmed the dissolution of cerium oxide. The intensified peak at 1086 cm⁻¹ and the appearance of additional peaks at 269 cm⁻¹ on spot 1 and 275 cm⁻¹ on the spot 2 demonstrate the growth of magnesium hydroxide.
Figure 7.14 The corrosion products analysis of the sample of Ce(IV)/(PEI/PAA)10 after 72 hours EIS tests. (a) The XRD pattern. (b) The Raman spectra.
Figure 7.15 The corrosion products analysis of the sample of Ce(IV)/PEI/GO/(PEI/PAA)10 after 72 hours EIS tests. (a) The XRD pattern. (b) The Raman spectra.
The sample of Ce(IV)/PEI/GO/(PEI/PAA)10 was also analyzed using XRD and Raman spectroscopy. Figure 7.15a illustrates the existence of peaks representing magnesium hydroxide on the XRD patterns of spot 1 and spot 2 of Ce(IV)/PEI/GO/(PEI/PAA)10. This result confirmed that the chemical composition of corrosion products of Ce(IV)/PEI/GO/(PEI/PAA)10 is also magnesium hydroxide. The XRD pattern of spot 3 on Ce(IV)/PEI/GO/(PEI/PAA)10 also shows a structure without corrosion products. However, none of the XRD patterns on Ce(IV)/PEI/GO/(PEI/PAA)10 had the peaks representing magnesium nitrate. This was due to the GO layer which prohibited the reaction between the nitric acid with the magnesium hydroxide during the deposition process. The sample of Ce(IV)/PEI/GO/(PEI/PAA)10 demonstrated a similar Raman features to that of Ce(IV)/(PEI/PAA)10 (Figure 7.15b). However, the combined peak at 460 cm\(^{-1}\) of cerium oxide and magnesium hydroxide on the spot 3 was closer to the standard cerium oxide peak and the peak at 1088 cm\(^{-1}\) was weaker. These results indicate that less magnesium hydroxide formed when GO was present. The peaks representing magnesium hydroxide were also present on spot 1 and spot 2 of Ce(IV)/PEI/GO/(PEI/PAA)10 while the combined peak shifted to 441 cm\(^{-1}\) on the spot 1. These results confirmed the growth of magnesium hydroxide on the surface of Ce(IV)/PEI/GO/(PEI/PAA)10 during the EIS test.

7.5.2. The protection mechanism of the multilayer coating

Both the observed corrosion products of the coatings prepared with and without GO were confirmed to be magnesium hydroxide but the mechanisms of degradation were different. The deterioration of the sample of Ce(IV)/(PEI/PAA)10 happened in three steps. When the weak pair of polyelectrolytes film was immersed in a diluted salt solution, the dissolving and formation of the film achieved equilibrium as follows [208]:

\[
\text{Pol}^+\text{Pol}^- + \text{Na}^+ + \text{Cl}^- \leftrightarrow \text{Pol}^+\text{Cl}^- + \text{Pol}^-\text{Na}^+
\]

(7.6)

where \(\text{Pol}^+\) and \(\text{Pol}^-\) represent the positively charged PEI and the negatively charged PAA. Therefore, the polyelectrolytes multilayer was considered as a buffering layer to the corrosive electrolytes [113]. However, with the increase of the immersion time and the NaCl concentration at the solution/coating interface, the equilibrium shifted to the right which indicates the decomposition of the polyelectrolyte multilayers [209]. Therefore, this shift was considered as a
sign of decomposition of the PEI/PAA multilayers (Figure 7.16a). After part of the PEI/PAA multilayer was decomposed, the corrosive electrolytes penetrated through the cracks of cerium based conversion layer to attack the magnesium substrate (Figure 7.16b). The dissolved magnesium ions then diffused out to the surface and formed magnesium hydroxide with the hydroxyl ions produced at the cathodic sites (Figure 7.16c). Therefore, the second and third degrading steps were the diffusion of anodized magnesium ions to the surface and the formation of magnesium hydroxide. The chemical reactions are as follows [23,210]:

Cathodic reactions:

\[
\begin{align*}
O_2 + 2H_2O + 4e^- & \rightarrow 4OH^- \quad (7.7) \\
2H_2O + 2e^- & \rightarrow 2OH^- + H_2 \uparrow \quad (7.8)
\end{align*}
\]

Anodic reaction:

\[
Mg \rightarrow Mg^{2+} + 2e^- \quad (7.9)
\]

Total reaction:

\[
Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \downarrow \quad (7.10)
\]

For the sample of Ce(IV)/PEI/GO/(PEI/PAA)10, the first step of degradation was also the decomposition of PEI/PAA multilayers (Figure 7.17a). However, the second and third degrading steps were slightly different from that of Ce(IV)/(PEI/PAA)10. The difference resulted from the incorporation of GO. The ideal graphene lattice prohibited the penetration of small ions because of its small pore diameter [136]. However, pure graphene cannot directly associate with the hydrophilic polymers. Therefore, GO was used in preparing this coating. Introducing the functional groups into graphene also induced defects into the graphene lattice. Therefore, some of the corrosive electrolytes penetrated through the defects of the GO layer (Figure 7.17b). After the formation of corrosion products, the intact GO sites formed a galvanic coupling with the corroded sites [211,212]. The presence of galvanic corrosion resulted in a faster corrosion reaction. However, the accelerated corrosion reaction formed a crack-free layer of magnesium hydroxide (Figure 7.17c). Compared with the cracked magnesium hydroxide layer on the sample of Ce(IV)/(PEI/PAA)10, this continuous layer of magnesium hydroxide passivated the surface and therefore provided a longer corrosion protection to the underlying substrate.
Figure 7.16 The protection mechanism of the sample of Ce(IV)/(PEI/PAA)10.
Figure 7.17 The protection mechanism of the sample of Ce(IV)/PEI/GO/(PEI/PAA)10.
7.6. Summary

In this Chapter, the graphene oxide (GO) layer was prepared in the middle of the cerium conversion layer and the poly(ethylene imine)/poly(acrylic acid) (PEI/PAA) multilayers. The scanning electron microscopy (SEM) images confirmed the high aspect ratio of GO which is essential for retarding the corrosion process. X-rays diffraction (XRD) and Raman spectroscopy were used to confirmed the deposition of GO in the sample. The 10 bilayers of PEI/PAA multilayers with GO demonstrated an excellent self-healing ability which was comparable to the 20 bilayers of PEI/PAA multilayers without GO. The hardness of the multilayers with GO dropped after water immersion. The absorbed water played a role of plasticizer which softened the PEI/PAA multilayers and induced the self-healing ability.

The corrosion resistance of the multilayer coatings with and without GO was tested using electrochemical impedance spectroscopy (EIS) at different times from 0.5 to 72 h. The results confirmed the anticorrosion ability of GO as the protection efficiency of the coating with GO stayed around 80% during all the times while the coating without GO decreased to ~40% after 72 h. The degradation processes of the multilayer coatings with and without GO were analyzed. The degradation process can be concluded into three steps:

(1) The PEI/PAA multilayers decomposed in the condensed salt solution.

(2) The cathodic and anodic corrosion reactions happened on the surface where the coating was dissolved.

(3) The corrosion products of = magnesium hydroxide formed on the surface.

The GO layer played a critical role in protecting the substrate as it accelerates the corrosion reactions in step 2 by forming a galvanic coupling. As a result, there formed a crack-free layer of magnesium hydroxide in step 3 which provided a better corrosion protection.
CHAPTER 8

THE APPLICATION OF PEI/PAA MULTILAYERS SELF-HEALING COATING ON ELECTROGALVANIZED STEEL

8.1. Overview

Both magnesium alloys and electrogalvanized steel (EGS) are necessary materials in the automotive industry [27,213]. If the poly(ethylene imine)/poly(acrylic acid) (PEI/PAA) multilayers can be applied on the EGS sample, the possibility of application of the multilayer self-healing coating in the automotive application will increase.

In Chapter 8, the preparation of the PEI/PAA multilayers on EGS via layer-by-layer (LbL) assembly was described. Because of the top zinc layer can react with poly(acrylic acid) during the multilayer preparation, the multilayers were directly deposited on the EGS surface without cerium conversion layer. The chemical structure of the multilayers using XRD and Raman spectroscopy was characterized.

The self-healing behavior of the multilayers on the EGS sample was confirmed by in-situ observation using the optical microscopy. The corrosion resistance of this multilayer coating was tested by electrochemical impedance spectroscopy (EIS). The samples of EGS with and without
the multilayer coating were characterized by SEM, EDS, XRD and Raman spectroscopy after the 72 h long EIS tests.

**8.2. Preparation and characterization of the PEI/PAA multilayers coating on EGS**

The EGS samples were obtained from ArcelorMittal. The steel substrates were coated with a zinc layer in their plants by electroplating. To remove the oil and dust on the as received EGS samples, the samples were washed with acetone in the ultrasonic bath machine for 10 minutes. Then, the bare EGS samples were immersed in the PEI solution for 5 min. The PEI solution was tuned to have a pH value of 9.5 with nitric acid. The samples were washed with the deionized water for 2 min. After that, the samples were immersed in the PAA solution for 5 min and finally washed with the deionized water for 2 min. The PAA solution was tuned to have a pH value of 4.5 with sodium hydroxide. This whole process was repeated for 20 times to prepare the multilayers coating on the EGS samples. These samples were denoted as (PEI/PAA)20.

SEM was used to observe the surface morphology of the EGS samples with and without the multilayers coating. Figure 8.1a shows that the bare EGS had a morphology which was similar to the piled tiles. This layer was generated from the electro-galvanic process during which the zinc layer was deposited on the steel surface. Figure 8.1b shows the polyelectrolytes coating deposited on the zinc surface via the layer-by-layer (LbL) deposition.

XRD and Raman spectroscopy were used to characterize the bare EGS and (PEI/PAA)20. The XRD patterns of bare EGS and (PEI/PAA)20 identified the zinc peaks at the two-theta angles of 55.3, 66.5 and 85.6 degrees (Figure 8.2a). This confirmed that the EGS samples were covered with zinc and the zinc layer remained during the LbL assembly. In addition, two weak peaks at 68.9 and 106.1 degrees representing iron were also identified. The XRD pattern of (PEI/PAA)20 had no significant peaks for the deposited polyelectrolytes. Therefore, Raman spectroscopy was applied to confirm the chemical structure of the polyelectrolytes deposited on the EGS samples. Also, Figure 8.2b shows that the Raman spectrum of bare EGS had no significant peaks. This was due to that Raman spectroscopy can only detect the vibration of covalent bonding. Because the bare EGS was composed of pure zinc and pure low carbon steel, there was no significant amount
of chemical bonding in the original samples. As a result, no peaks appeared in the Raman spectrum of bare EGS. On the contrary, multiple peaks on the sample of (PEI/PAA)$_{20}$ (Figure 8.2b) were observed.

Figure 8.1 SEM images of (a) bare EGS and (b) (PEI/PAA)$_{20}$. 
Figure 8.2 The XRD patterns and Raman spectra of bare EGS and (PEI/PAA)20. (a) The XRD patterns. (b) The Raman spectra.
The Raman shift at 382 cm\textsuperscript{-1} demonstrated the C-O symmetric stretching of ZnCO\textsubscript{3} [213]. The corrosion products of ZnCO\textsubscript{3} was generated during the LbL assembly which strengthened the binding of the zinc layer and the polyelectrolyte multilayers. The peak at 892 cm\textsuperscript{-1} represented the NH\textsubscript{2} wagging and twisting vibration from the PEI molecular chains [163]. The Raman shift at 1521 cm\textsuperscript{-1} represented the symmetric NH\textsubscript{3}\textsuperscript{+} deformation [182]. These results confirmed the deposition of PEI on the surface. The peak at 1402 cm\textsuperscript{-1} stood for the C-OH vibration of the C-OH group from the PAA molecular chains [194]. The peak at 1739 cm\textsuperscript{-1} represented the C=O stretching deformation of the PAA molecular chains [47]. These results confirmed the deposition of PAA on the sample surface. Furthermore, the peaks at 1310 cm\textsuperscript{-1} and 1447 cm\textsuperscript{-1} represented the C-H\textsubscript{2} wagging and C-H\textsubscript{2} bending of the molecular chains, respectively [182].

8.3. The self-healing behavior of the PEI/PAA multilayers coating on EGS

The sample of (PEI/PAA)\textsubscript{20} was expected to demonstrate a self-healing ability on steel as on the samples of magnesium alloys. Optical microscopy was used to confirm the self-healing ability of (PEI/PAA)\textsubscript{20}. The samples were mounted on the stage of a Nikon optical microscope by tapes. The microscope was connected to the PAX-it system which recorded the images. The magnification was 50. A scalpel was used to make cuts on the sample surface. A water droplet was dropped on the cut surface using a pipette. After 10 min, the water was absorbed by a KIMTECH wiper and dried using a Fresherband lint and dust remover. Figure 8.3a shows the cut was made on the surface using a scalpel. A water droplet was dropped on the surface. After 10 min, the surface was dried with lab wipers and a lint remover. The same spot on the surface was observed and it was found that the cut disappeared (Figure 8.3b). This result agreed with the healing observed on the magnesium alloys coated with 20 bilayers of PEI and PAA. This self-healing ability was also better than that observed on the magnesium alloys coated with 20 bilayers of PEI and PAA. The better self-healing ability was induced by the higher flexibility of molecular chains discussed in Chapter 6. Furthermore, the self-healing ability of (PEI/PAA)\textsubscript{20} was tested for multiple cuts. Figure 8.3c shows three cuts on the surface made using a scalpel. Then, a water droplet was dropped on the surface. After 10 min, the surface was dried. The same spot on the surface was observed and it was found that all the cuts disappeared (Figure 8.3d). This result confirmed the excellent self-healing ability of (PEI/PAA)\textsubscript{20} in the case of multiple cuts.
The corrosion resistance of the PEI/PAA multilayers coating on EGS was used to test the corrosion resistance of the bare EGS and (PEI/PAA)\textsuperscript{20} for different immersing times. The samples were immersed in a 3.5 wt.% NaCl solution and applied the EIS tests at 0.5, 2, 4, 24, 48 and 72 h. Figure 8.4 to Figure 8.6 shows the Bode impedance and Nyquist plots of the EIS results. After 0.5 h immersion, there was only one capacitive response from the bare EGS at the intermediate frequency region (Figure 8.4a). This was due to the double layer at the interface between the NaCl solution and the EGS surface. On the contrary, there were two capacitive responses merged together at the intermediate frequencies from the sample of (PEI/PAA)\textsuperscript{20} (Figure 8.4a). These two capacitive responses were to the interface between the solution and the coating surface and the interface between the coating and the EGS surface. Because a pure capacitance was expected to exhibit a Bode phase of -90
degrees, the defect and degradation of the polyelectrolyte coating weakened the Bode phase of the capacitive response from a real system [202]. The capacitive response of (PEI/PAA)20 was close to -60 degrees while the capacitive response of bare EGS was around -40 degrees. This result confirmed the improved corrosion resistance by the PEI/PAA multilayers. In addition, because the impedance of the capacitance was defined as: \( Z_c = \frac{1}{j2\pi fC} \), where \( f \) is the frequency [214]. A lower frequency of the capacitance leads to a higher impedance. The capacitive response from (PEI/PAA)20 was at the frequency lower than that from the bare EGS. This result also confirmed the better corrosion resistance of (PEI/PAA)20. After 2 h immersion, there was another capacitive response from the bare EGS which was possibly due to the zinc corrosion products formed on the surface (Figure 8.4b). In addition, the capacitive responses from the bare EGS degraded with a weaker capacitive response at Bode phase of -35 degrees. This degradation confirmed the corrosion of the zinc layer which decreased the corrosion resistance of the bare EGS. However, the capacitive responses from the sample of (PEI/PAA)20 was stable (Figure 8.4b). This result demonstrates a good corrosion resistance of the PEI and PAA multilayers. Figure 8.4c shows that with time the capacitive responses from the sample of (PEI/PAA)20 shifted to a lower frequency. This was attributed to the decrease of the permittivity of the coating by precipitation of the corrosion products [203,204]. The capacitive response from the bare EGS degraded further with a weaker capacitive response at -30 degrees. After 24 h immersion, the degradation of both samples were observed (Figure 8.4d). The third capacitive response from the bare EGS appeared at the low frequency region. Meanwhile, the capacitive responses from the sample of (PEI/PAA)20 degraded with a weaker capacitive response at Bode phase of -50 degrees. After 48 h immersion, the capacitive responses from the sample of (PEI/PAA)20 became broader with a Bode phase of -40 degrees (Figure 8.4e). The third capacitive responses from the bare EGS separated from the capacitive responses at the intermediate frequency region (Figure 8.4e). After 72 h immersion, the third capacitive response from the sample of (PEI/PAA)20 appeared at the intermediate frequency region and merged with the other two capacitive responses (Figure 8.4f). Meanwhile, the third capacitive responses from the bare EGS became more significant at the high frequency region (Figure 8.4f).

After 0.5 h immersion, the Bode impedance of (PEI/PAA)20 showed an impedance of 600 \( \Omega \cdot \text{cm}^2 \) while the Bode impedance of the bare EGS demonstrated an impedance of 100 \( \Omega \cdot \text{cm}^2 \) (Figure 8.5a). The Bode impedance of (PEI/PAA)20 after immersion of 2 and 4 h showed the same feature
as that of 0.5 h exposure (Figure 8.5b and c). These results agreed with the Bode phases registered for (PEI/PAA)20 after immersion of 4h. After 24 h immersion, the Bode impedance of (PEI/PAA)20 decreased to 300 Ω·cm² while the Bode impedance of (PEI/PAA)20 decreased to less than 100 Ω·cm² (Figure 8.5d). After 48 h immersion, the Bode impedance of (PEI/PAA)20 slightly reduced to less than 300 Ω·cm² (Figure 8.5e). The Bode impedance of bare EGS increased to values higher than 100 Ω·cm² (Figure 8.5e). After 72 h immersion, the Bode impedance stayed around 300 Ω·cm² which confirmed the accumulation of corrosion products (Figure 8.5f). These corrosion products generated the third capacitive response from the sample of (PEI/PAA)20. The Bode impedance of bare EGS further increased to 400 Ω·cm² (Figure 8.5f). This increase of impedance was probably due to the accumulation of corrosion products which acted as a barrier to the corrosive medium. All these features of change were observed in the Nyquist plots (Figure 8.6). The radii of the circles in the Nyquist plots of bare EGS and (PEI/PAA)20 stayed stable from 0.5 to 4 h without significant decrease (Figure 8.6a - c). After 24 h immersion, the diameter of the circles in the Nyquist plots of bare EGS and (PEI/PAA)20 decreased (Figure 8.6d). After 48 h immersion, the diameter of the circles of (PEI/PAA)20 further reduced while the diameter of the circles of bare EGS was increased (Figure 8.6e). This increased diameter also confirmed the barrier property of the corrosion products. The diameter of the circles of bare EGS further increased after 72 h immersion (Figure 8.6f). This result confirmed the growth of the corrosion products which further protected the substrate.
Figure 8.4 The Bode phases of the EIS results at (a) 0.5 h, (b) 2 h, (c) 4 h, (d) 24 h, (e) 48 h and (f) 72 h.
Figure 8.5 The Bode impedance of the EIS results at (a) 0.5 h, (b) 2 h, (c) 4 h, (d) 24 h, (e) 48 h and (f) 72 h.
Figure 8.6 The Nyquist plots of the EIS results at (a) 0.5 h, (b) 2 h, (c) 4 h, (d) 24 h, (e) 48 h and (f) 72 h.
To quantify the corrosion resistance of bare EGS and (PEI/PAA)20, three equivalent circuits were used to fit the EIS results (Figure 8.7). The $R_s$ represents the corrosion resistance of the solution. The $Q_{dl}$ represents the constant phase of the double layer. Constant phase element (CPE) was used to replace the capacitance due to the non-ideal capacitive response. The impedance of a constant phase was defined as: $Z_{CPE} = Y_0^{-1} (j\omega)^{-n}$, where $Y_0$ is the admittance constant of the constant phase ($\Omega^{-1} \cdot s^n/cm^2$), $\omega$ is the angular frequency ($rad \cdot s^{-1}$), and $n$ is the constant phase exponent [215]. $R_{ct}$ represents the charge transfer resistance at the electrode. The $Q_1$ and $Q_2$ stand for the capacitive behavior of the coatings and the corrosion products while the $R_1$ and $R_2$ stand for the resistive behavior of the coatings and the corrosion products. Because there was only one capacitive response for the bare EGS at 0.5 h, the equivalent circuit with one parallel resistor and CPE (model 1) was applied to fit the EIS result at 0.5 h of bare EGS (Figure 8.7a). The equivalent circuit with two parallel resistor and CPE (model) was used to fit the EIS results of bare EGS from 2 to 4 h and the EIS result of (PEI/PAA)20 from 0.5 to 48 h because both samples demonstrated two capacitive responses during this period (Figure 8.7b). The equivalent circuit with three parallel resistor and CPE (model 3) was used to fit the EIS results of bare EGS from 24 to 72 h and the EIS result of (PEI/PAA)20 at 72 h because of the appearance of the third capacitive response in both samples (Figure 8.7c). All the fitted results are shown in Table 8.1.

![Equivalent circuits](image)

Figure 8.7 The equivalent circuits for the EIS results. (a) Model 1. (b) Model 2. (c) Model 3.
To compare the corrosion resistance of bare EGS and (PEI/PAA)20 at different immersion times, the polarization resistance ($R_p$) was calculated by the following equations:

\[
\text{model 1: } \frac{1}{R_p} = \frac{1}{R_{ct}} \tag{8.1}
\]

\[
\text{model 2: } \frac{1}{R_p} = \frac{1}{R_{ct} + R_1} \tag{8.2}
\]

\[
\text{model 3: } \frac{1}{R_p} = \frac{1}{R_{ct} + R_1 + R_2} \tag{8.3}
\]

Figure 8.8 shows that the polarization resistance of bare EGS stayed around 100 $\Omega \cdot \text{cm}^2$ due to the corrosion of zinc which protected the underlying steel. However, with the corrosion of iron and the generated corrosion products, the polarization resistance of bare EGS increased to 400 $\Omega \cdot \text{cm}^2$ after 72 h. On the contrary, the polarization resistance of the sample of (PEI/PAA)20 continuously decreased from 800 to 250 $\Omega \cdot \text{cm}^2$ during the times from 0.5 h to 48 h due to the dissolving of the PEI and PAA multilayers. The polarization resistance of (PEI/PAA)20 also increased to 400 $\Omega \cdot \text{cm}^2$ due to the formation of corrosion products of zinc which strengthened the corrosion protection.

![Figure 8.8 The polarization resistance of bare EGS and (PEI/PAA)20.](image)
<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Rs (Ω·cm²)</th>
<th>Ω·cm²</th>
<th>Sample (PEI/PAA)20</th>
<th>Bare EGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>18.56E-3</td>
<td>0.2</td>
<td>8.97E-3</td>
<td>234.40</td>
</tr>
<tr>
<td>0.3</td>
<td>10.83E-3</td>
<td>0.3</td>
<td>8.90E-3</td>
<td>317.20</td>
</tr>
<tr>
<td>0.4</td>
<td>6.00E-3</td>
<td>0.4</td>
<td>16.00E-3</td>
<td>64.17E-3</td>
</tr>
<tr>
<td>0.5</td>
<td>3.38E-3</td>
<td>0.5</td>
<td>8.64E-3</td>
<td>23.84E-3</td>
</tr>
<tr>
<td>0.6</td>
<td>2.13E-3</td>
<td>0.6</td>
<td>10.26E-3</td>
<td>42.56E-3</td>
</tr>
<tr>
<td>0.7</td>
<td>1.40E-3</td>
<td>0.7</td>
<td>7.86E-3</td>
<td>8.56E-3</td>
</tr>
<tr>
<td>0.8</td>
<td>0.87E-3</td>
<td>0.8</td>
<td>5.36E-3</td>
<td>5.40E-3</td>
</tr>
<tr>
<td>0.9</td>
<td>0.50E-3</td>
<td>0.9</td>
<td>3.13E-3</td>
<td>2.56E-3</td>
</tr>
<tr>
<td>1</td>
<td>0.34E-3</td>
<td>1.0</td>
<td>1.63E-3</td>
<td>0.34E-3</td>
</tr>
</tbody>
</table>

Table 8.1: Fitted EIS data for bare EGS and (PEI/PAA)20
8.5. The analysis of the corrosion products on bare EGS and (PEI/PAA)20

After the 72 h EIS tests, two different spots were found on the sample of bare EGS and (PEI/PAA)20. Therefore, SEM, EDS, XRD and Raman spectroscopy were used to identify the different chemical compositions of these different spots. Figure 8.9 shows that the sample of bare EGS was mainly composed of carbon, oxygen, zinc, iron, sodium and chloride after the EIS tests. On the lightly corroded spot, some small islands formed on the surface (Figure 8.9a). The EDS map scanning demonstrated that these islands consisted of sodium, carbon, and oxygen. As a result, these islands could be sodium carbonate which was formed by the sodium ions from the sodium salt with the carbonate ions from the dissolved carbon dioxide. Meanwhile, the zinc and iron
distributed evenly on the surface. The atomic ratio of iron only accounted for 1.7% at the lightly corrode spot. Figure 8.9b shows the SEM and EDS images of the heavily corroded spots on the sample of bare EGS. The amount of sodium carbonate islands increased and covered an additional area of the surface. In addition, cracks happened on the surface. The EDS map scanning shows that the cracked surface was the zinc layer while more iron was observed in the cracks. The atomic ratio of iron increased to 5.3% on this spot. With the development of corrosion reaction, the zinc layer was sacrificed to protect the underlying iron substrate. When the iron substrate was exposed, the zinc layer lost the protection to the substrate and the corrosive electrolytes attacked the iron substrate to form iron oxides.

Figure 8.10 The SEM and EDS images of lightly and heavily corroded spots on (PEI/PAA)20. (a) Lightly corroded spot. (b) Heavily corroded spot.
Figure 8.10 shows the SEM and EDS images of the lightly and heavily corroded spots on the sample of (PEI/PAA)20. Nitrogen became significant on the surface because it is the essential element of PEI. In addition, the amount of carbon doubled that observed in bare EGS. This result confirmed the existence of PEI/PAA multilayers after EIS tests because carbon is the fundamental elements of both PAA and PEI. Some small islands were entrapped in the PEI/PAA multilayer coating. The EDS map demonstrated that these islands were mainly composed of sodium and chloride (Figure 8.10a) and this result agreed with the previous model that the PEI/PAA multilayer acted as a buffering layer. This buffering layer absorbed and stopped the penetration of the salt [113]. The SEM image of the lightly corroded spot shows that the PEI/PAA multilayer coating cracked (Figure 8.10a). This was possibly due to the crack of the zinc layer and the absorption of salt which induced additional stress to the multilayers. With the advancing of corrosion, the islands of corrosion products grew on the surface (Figure 8.10b). The EDS map scanning shows that the islands on the surface were composed of sodium, carbon, and oxygen. More zinc was recorded as the atomic ratio of zinc increased from 3.0% to 22.6%. The amount of nitrogen decreased to 0.2% indicating the dissolving of the PEI/PAA multilayers. However, the atomic percentage of iron was 0.3% which was negligible. This result shows that the iron substrate of (PEI/PAA)20 was still under protection after 72 h EIS tests. The atomic percentage of EDS results are shown in Table 8.2.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Bare EGS (lightly corroded)</th>
<th>Bare EGS (heavily corroded)</th>
<th>(PEI/PAA)20 (lightly corroded)</th>
<th>(PEI/PAA)20 (heavily corroded)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>23.1 At%</td>
<td>24.5 At%</td>
<td>3.0 At%</td>
<td>22.6 At%</td>
</tr>
<tr>
<td>Fe</td>
<td>1.7 At%</td>
<td>5.3 At%</td>
<td>0</td>
<td>0.3 At%</td>
</tr>
<tr>
<td>O</td>
<td>46.2 At%</td>
<td>42.7 At%</td>
<td>11.5 At%</td>
<td>29.0 At%</td>
</tr>
<tr>
<td>C</td>
<td>23.9 At%</td>
<td>22.4 At%</td>
<td>54.5 At%</td>
<td>24.3 At%</td>
</tr>
<tr>
<td>Na</td>
<td>4.5 At%</td>
<td>4.6 At%</td>
<td>9.9 At%</td>
<td>15.5 At%</td>
</tr>
<tr>
<td>Cl</td>
<td>0.6 At%</td>
<td>0.5 At%</td>
<td>8.4 At%</td>
<td>8.1 At%</td>
</tr>
<tr>
<td>N</td>
<td>0</td>
<td>0</td>
<td>12.7 At%</td>
<td>0.2 At%</td>
</tr>
</tbody>
</table>

Table 8.2 EDS results for bare EGS and (PEI/PAA)20 after 72 h EIS tests
Figure 8.11 The XRD patterns and Raman spectra of lightly corroded and heavily corroded spots on the sample of bare EGS. (a) XRD patterns. (b) Raman spectra.
Figure 8.11 shows the XRD patterns and Raman spectra of the sample of bare EGS after EIS tests. All the bands' assignment of the Raman spectra is shown in Table 8.3. Because the lightly corroded spot was black, the XRD and Raman results were denoted as bare EGS-72hrs-black. In addition, because the heavily corrode spot was white, the XRD and Raman results were indicated as bare EGS-72hrs-white. Figure 8.11a shows that the most significant peaks of XRD transferred from zinc peaks to iron peaks. This result indicates that the zinc layer was depleted during the EIS tests. In addition, it was found that the main corrosion products were zinc hydroxide and maghemite (γ-Fe₂O₃). With the progress of corrosion, more peaks appeared in the XRD pattern. The peaks representing sodium carbonate were observed. This result agreed with the EDS map scanning. In addition, the zinc oxide and zinc carbonate were also observed. These results confirmed that the zinc layer acted as a sacrificial layer which protected the underlying iron substrate. Figure 8.11b shows the Raman spectra of the bare and coated EGS. The Raman shifts at 205 cm⁻¹ and 318 cm⁻¹ demonstrated the structure of the dense oxygen packing of zinc hydroxide [213]. The peak at 426 cm⁻¹ stood for the zinc oxide while the peak at 544 cm⁻¹ represented the Fe-O (Fe²⁺) bonding [213]. The 739 cm⁻¹ observed on heavily corroded spot represented the Fe-O (Fe³⁺) bonding which indicated the further oxidation of iron. Both the peak at 1066 cm⁻¹ and 1332 cm⁻¹ on the heavily corroded spot were stronger than the peaks at 1074 cm⁻¹ and 1321 cm⁻¹ on the heavily corroded spot. Because these peaks respectively represented the C-O bending of zinc carbonate and iron oxide [213,216], more corrosion products were produced on the heavily corroded spot.

Figure 8.12 shows the XRD patterns and Raman spectra of the sample of (PEI/PAA)20 after EIS tests. Because the lightly corroded spot was gray, the XRD and Raman results were denoted as (PEI/PAA)20-72hrs-grey. In addition, because the heavily corrode spot was white, the XRD and Raman results were denoted as (PEI/PAA)20-72hrs-white. Figure 8.12a shows that all the most significant peaks in the XRD pattern were the zinc peaks. This result was different from the sample of bare EGS and confirmed the protection effect of the PEI/PAA multilayers which delayed the dissolving of the zinc layer. It was found that zinc oxide and zinc hydroxide were the main corrosion products on the lightly corroded spot of (PEI/PAA)20. The absence of maghemite peaks further proves the better corrosion resistance of the multilayer coating. The sodium carbonate on the heavily corroded spot of (PEI/PAA)20 was observed. This result agreed with the result of EDS map scanning which demonstrated the growth of sodium carbonate on the surface. Figure 8.12b compares the Raman spectra of the corroded and non-corroded samples of (PEI/PAA)20. The
Raman shift around 400 cm$^{-1}$ intensified from the non-corrode sample to the lightly and heavily corroded spot. Because this peak stood for the C-O stretching of zinc carbonate, the stronger peak indicated the progression of corrosion products of zinc. In addition, the peak representing Fe-O (Fe$^{2+}$) bonding at 555 cm$^{-1}$ and 549 cm$^{-1}$ on the non-corroded and lightly corroded spot of (PEI/PAA)$_{20}$ disappeared while the peak representing the Fe-O (Fe$^{3+}$) at 755 cm$^{-1}$ appeared on the heavily corroded spot of (PEI/PAA)$_{20}$. This result confirmed the additional oxidation of iron. The iron oxidation bonds appeared on the Raman spectrum but the oxide diffraction peaks disappeared. This was due to the different working mechanisms of XRD and Raman spectroscopy. The XRD can only detect the crystallized materials while the Raman spectroscopy can detect the chemical bonding. Therefore, Raman spectroscopy is more sensitive to a few oxidants. In addition, the functional groups including the C=O stretching deformation at 1739 cm$^{-1}$ and the symmetric NH$_3^+$ deformation at 1521 cm$^{-1}$ disappeared on the corroded spot. This result confirmed the dissolving of the PEI/PAA multilayers which consumed the functional groups of the polyelectrolytes. However, the peaks at ~1447 cm$^{-1}$, ~2886 cm$^{-1}$ and ~2926 cm$^{-1}$ representing the vibration of C-H$_2$ bonding intensified on the corroded spots. This was due to the property of the backbones of the molecular chains which were stable with the corrosive electrolytes.
Figure 8.12 The XRD patterns and Raman spectra of lightly corroded and heavily corroded spots on the sample of (PEI/PAA)20. (a) XRD patterns. (b) Raman spectra.
Table 8.3 The Raman bands assignment of bare EGS and (PEI/PAA)20 after 72 h EIS tests

<table>
<thead>
<tr>
<th>Bare EGS</th>
<th>Bare EGS-72hrs-white</th>
<th>(PEI/PAA)20-72hrs-grey</th>
<th>(PEI/PAA)20-72hrs-grey</th>
<th>(PEI/PAA)20-72hrs-white</th>
<th>Bands assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>205</td>
<td>235</td>
<td>236</td>
<td>210</td>
<td>284</td>
<td>The layer structure made of the dense oxygen packing including goethite ($\alpha$-FeOOH), lepidocrocite ($\gamma$-FeOOH), ZnCO$_3$, Zn(OH)$_2$ [213].</td>
</tr>
<tr>
<td>318</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>The C-O symmetric stretching of ZnCO$_3$ [213]</td>
</tr>
<tr>
<td>382</td>
<td>393</td>
<td>404</td>
<td>405</td>
<td></td>
<td>ZnO [213]</td>
</tr>
<tr>
<td>426</td>
<td>555</td>
<td>549</td>
<td>545</td>
<td>755</td>
<td>Fe-O ($\text{Fe}^{3+}$) [213]</td>
</tr>
<tr>
<td>446</td>
<td>549</td>
<td>545</td>
<td>545</td>
<td>755</td>
<td>Fe-O ($\text{Fe}^{3+}$) [213]</td>
</tr>
<tr>
<td>544</td>
<td>739</td>
<td>897</td>
<td>890</td>
<td>892</td>
<td>NH$_2$ wagging and twisting vibration [163]</td>
</tr>
<tr>
<td>1074</td>
<td>1066</td>
<td></td>
<td></td>
<td></td>
<td>The C-O bending of ZnCO$_3$ [213]</td>
</tr>
<tr>
<td>1099</td>
<td>1097</td>
<td>1092</td>
<td></td>
<td></td>
<td>The C-O bending of CO$_3^{2-}$ [213]</td>
</tr>
<tr>
<td>1201</td>
<td>1194</td>
<td>1273</td>
<td></td>
<td></td>
<td>C-O [163]</td>
</tr>
<tr>
<td>1310</td>
<td>1305</td>
<td>1273</td>
<td></td>
<td></td>
<td>CO$_3^{2-}$ [213]</td>
</tr>
<tr>
<td>1321</td>
<td>1332</td>
<td>1321</td>
<td></td>
<td></td>
<td>C-H$_2$ wagging [182]</td>
</tr>
<tr>
<td>1402</td>
<td>1407</td>
<td>1321</td>
<td></td>
<td></td>
<td>Fe$_2$O$_3$ [216]</td>
</tr>
<tr>
<td>1447</td>
<td>1450</td>
<td>1459</td>
<td></td>
<td></td>
<td>O-H vibration of the C-OH group [194]</td>
</tr>
<tr>
<td>1521</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Symmetric NH$_3^+$ deformation [182]</td>
</tr>
<tr>
<td>1739</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C=O stretching deformation [47]</td>
</tr>
<tr>
<td>2886</td>
<td>2882</td>
<td></td>
<td></td>
<td></td>
<td>C-H$_2$ stretching vibration [163]</td>
</tr>
<tr>
<td>2926</td>
<td>2926</td>
<td></td>
<td></td>
<td></td>
<td>C-H$_2$ stretching vibration [163]</td>
</tr>
</tbody>
</table>
8.6. The degrading process of bare EGS and (PEI/PAA)20

SEM was used to observe the surface of bare EGS and (PEI/PAA)20 after EIS tests. Different morphologies of corroding products were found in the sample with and without coating. Figure 8.13 shows the degrading process of the sample of bare EGS. Figure 8.13a shows the morphology of the bare EGS. Because the zinc layer was applied to be the sacrificial layer to protect the iron substrate, it started to dissolve in the corrosive environment. Figure 8.13b shows that the characteristic initial morphology diminished. Then, the corrosion products began to grow on the surface (Figure 8.13c). The corrosion products of zinc cannot be identified on the surface but the small islands of sodium carbonate were very clear. Finally, the corrosion products of sodium carbonate covered a large area of the surface and cracks happened on the zinc surface (Figure 8.13d). The corrosive electrolytes penetrated through the cracks to react with the iron substrate.

Figure 8.13 The degrading process of bare EGS. (a) The intact bare EGS. (b) The zinc layer started to dissolve. (c) The corrosion product of sodium carbonate started to grow. (d) The crack initiated on the zinc layer.
Figure 8.14 shows the degrading process of the sample of (PEI/PAA)20. Figure 8.14a shows the morphology of the sample of (PEI/PAA)20 before it was exposed to corrosion attack. The layer of coating started to dissolve in the presence of concentrated salt solution because the equilibrium of polyelectrolyte charge was broken by the salt ions [209]. Figure 8.14b shows that the surface of (PEI/PAA)20 became flat without any prominent feature. Then, cracks were initiated on the surface due to the absorption of salt ions (Figure 8.14c). The corrosive electrolytes penetrated through the cracks and reacted with zinc. Figure 8.14d shows that the cracks grew bigger and the corrosion products of sodium carbonate were generated on the surface.

Figure 8.14 The degrading process of (PEI/PAA)20. (a) The intact (PEI/PAA)20. (b) The PEI/PAA multilayers started to dissolve. (c) The crack initiated on the PEI/PAA multilayers. (d) The crack grew and the corrosion products formed on the surface.
8.7. Summary

20 bilayers of poly(ethylene imine)/poly(acrylic acid) (PEI/PAA) were prepared directly on the EGS surface without the cerium conversion layer. The X-rays diffraction (XRD) pattern confirmed the existence of the zinc layer on the EGS sample. The Raman spectrum demonstrated the successful deposition of the PEI/PAA multilayers on the electrogalvanized steel (EGS) sample.

A single cut and the multiple cuts were made on the sample surface using a scalpel. The sample exhibited an excellent self-healing ability which healed both the single cut and the multiple cuts after it was immersed in water for 10 min.

The electrochemical impedance spectroscopy (EIS) results show that the sample coated with the PEI/PAA multilayers had a better corrosion resistance than that of the EGS sample before 48 h of immersion. However, the corrosion resistance of the bare EGS sample became better that of the sample of (PEI/PAA)20 after 72 h of immersion in corrosive solution. This was due to the degradation of the multilayers and the formation of the corrosion products which passivated the bare EGS surface. The samples after 72 h EIS tests were characterized. The results show that underlying iron substrate of the bare EGS was corroded by the corrosive electrolytes. However, the PEI/PAA multilayers protected the iron substrate from corrosion by absorbing the corrosive electrolytes and stopping their penetration to the substrate.

In conclusion, this PEI/PAA self-healing multilayer coating provided an extended corrosion protection to the electrogalvanized steel.
CHAPTER 9

CONCLUSIONS AND FUTURE WORK

9.1. Summary and Conclusions

In this thesis, the acrylic elastomer, VHB 4910, and the multilayer polyelectrolyte coating were studied. The objectives of this study were completed as follows:

The chemical structure of the acrylic elastomer was analyzed by X-rays diffraction (XRD) and Raman spectroscopy. It was confirmed that the acrylic elastomer had an amorphous structure which has lower constraints on the mobility of molecular chains. In addition, the Raman spectrum confirmed the existence of carbonyl bonds which are characteristic for acrylic materials.

The unidirectional tensile tests showed that this acrylic elastomer had an extraordinary mechanical strength with a fracture strain around 9. It was found that the fracture stress increased and the fracture strain decreased with the increase of deformation speeds. This was due to the viscoelastic property of this material. In addition, this material demonstrated a hysteresis behavior during the cyclic tensile tests. The hysteresis behavior was attributed to the energy dissipation by the dissociation of non-covalent bonding. Reversibility of the non-covalent bonding was confirmed by the ability of self-recovery of the hysteresis behavior.
To further confirm the existence of the non-covalent bonding, the self-healing ability of this material was tested by cutting the sample into two parts and then brought them together. It was demonstrated that this material had a good self-healing ability which increased with the healing time and temperature. The self-healing efficiency of this material reached to ~70% under room temperature and ~120% under an elevated temperature of 120 degrees Celsius.

The Raman spectra confirmed that the hydrogen bonding at the interface between two separated parts contributed to the self-healing behavior. In addition, the theoretical calculation of the fracture stresses indicates that the diffusion of molecular chains also contributed to the self-healing process. Therefore, it can be concluded that both the hydrogen bonding and molecular chain diffusion were responsible for the self-healing ability of the acrylic elastomer.

Because the acrylic elastomer cannot be dissolved in any solvents, the self-healing coating on magnesium was prepared using the poly(acrylic acid) which had a similar chemical structure to the acrylic elastomer. The self-healing coating was fabricated via layer-by-layer (LbL) assembly of poly(acrylic acid) and poly(ethylene imine). The magnesium sample was pretreated with the cerium nitrate solution to form a conversion layer of cerium compounds. This conversion layer strengthened the bonding between the magnesium substrate and the polymeric coating and provided corrosion protection to the substrate.

A cut on the coating surface was made and a water droplet was dropped on the damaged area. It was found that the cut disappeared after 10 minutes. This result confirmed the self-healing ability of this coating. The swelling tests showed that the water absorption of the polyelectrolytes increased with time and depended on the number of layers of polyelectrolytes. Therefore, it was the swelling behavior in the presence of water that healed the cut.

Graphene oxide was added to the multilayer coating to improve the corrosion resistance. The corrosion resistances of the sample of bare magnesium alloy, the sample coated with the polyelectrolytes only and the sample coated with polyelectrolytes and graphene oxide were tested. The electrochemical impedance spectroscopy results showed that the sample coated with polyelectrolytes and graphene oxide demonstrated the best corrosion resistance during 72 hours’ tests. Both the polyelectrolytes and the graphene oxide provided corrosion protection to the magnesium substrate.
In addition, the polyelectrolytes coating was applied to the galvanized steel. The coating on the galvanized steel also showed the self-healing ability in the presence of water. The corrosion resistance of the galvanized steel was improved by the polyelectrolyte coating as well. The presented applications confirmed the versatility of the developed coating. Because both magnesium alloys and galvanized steels were used in automotive manufacture, this coating had a potential to be applied in the automotive industry.

### 9.2. Contributions to original knowledge

- **The self-healing ability of the acrylic elastomer**
  
  The self-healing ability of the acrylic elastomer was first reported by us. Because this material has been used in actuators and artificial muscles, the discovery of the self-healing ability can stimulate other applications of this material.

- **The self-healing mechanism of the acrylic elastomer**
  
  The self-healing mechanism of the acrylic elastomer was reported by us for the first time. This material achieved a good balance of mechanical strength and self-healing ability. The self-healing mechanism proposed for this material can contribute to the design of self-healing materials in the future.

- **The fabrication of the self-healing anticorrosion coating on magnesium alloy**
  
  To our best knowledge, this was the first polyelectrolyte coating prepared on magnesium alloys. Because of the high sensitivity of magnesium to corrosive medium, the polyelectrolyte with acidic pH value cannot be used as the coating. However, in this thesis the cerium conversion layer was combined with the polyelectrolytes and the polyelectrolytes coating on the magnesium alloy was successfully fabricated. In addition, this coating demonstrated a rapid self-healing ability in the presence of water and improved the corrosion resistance by 2 orders compared with the bare magnesium alloys.

- **The role of graphene oxide in self-healing and corrosion resistance**
  
  The graphene oxide was added to the multilayer coating to provide an additional corrosion protection. This novel coating had a better self-healing ability and much better corrosion resistance than the coating without the graphene oxide.
9.3. Future works

Most of the study of the acrylic elastomers was conducted on actuators because of special dielectric properties. Only the self-healing ability of its mechanical strength was tested. Therefore, it is worth to test the self-healing ability of dielectric property.

Because this polyelectrolyte multilayer coating was confirmed to be a self-healing, it may be developed for various applications. However, because of the hydrophilic nature of the polyelectrolytes, the coating can be easily contaminated. Therefore, another superhydrophobic layer should be applied to provide the self-cleaning ability. Furthermore, the model that establishes the relationship between the maximum self-healing ability and the swelling ratio should be developed in the future.

In addition, the preparation method of dip coating required a long processing time which is not cost effective. Therefore, using spray coating or spin coating could possibly be adopted. Many factors are expected to influence the property of the polyelectrolyte coating including the pH value, temperature, ionic strength, molecular weight and solvent quality. The future work could consider studying the influence of these parameters on the quality of this coating. In summary, the future work is required to fabricate the coating with a good quality in a short time.

The graphene oxide was added to the coating. However, the existence of defects in the graphene oxide is a latent risk for the corrosion protection. Therefore, combining the reduced graphene oxide with the polyelectrolytes could be a solution because the reduced graphene oxide is defect free. However, the absence of functional groups of the reduced graphene oxide complicates the development of such coating.
REFERENCES


[12] R. Pelrine, High-Speed Electrically Actuated Elastomers with Strain Greater Than 100%,


[101] K. Aramaki, Self-healing mechanism of an organosiloxane polymer film containing sodium
silicate and cerium(III) nitrate for corrosion of scratched zinc surface in 0.5 M NaCl, Corros. Sci. 44 (2002) 1621–1632.


[131] C. Cheng, N. White, H. Shi, M. Robson, M.L. Bruening, Cation separations in electrodialysis through membranes coated with polyelectrolyte multilayers, Polymer


[154] D.E. Bergbreiter, K. Liao, Covalent layer-by-layer assembly—an effective, forgiving way


[186] M. Huang, J. Yang, Facile microencapsulation of HDI for self-healing anticorrosion


[205] L.G. Bland, A.D. King, N. Birbilis, J.R. Scully, Assessing the Corrosion of Commercially Pure Magnesium and Commercial AZ31B by Electrochemical Impedance, Mass-Loss,


[215] A. Pepe, M. Aparicio, A. Durán, S. Ceré, Cerium hybrid silica coatings on stainless steel

APPENDIX

The Copyright and permission for reusing the context, figures, and tables of “F. Fan, J. Szpunar, Characterization of viscoelasticity and self-healing ability of VHB 4910. Macromolecular Materials and Engineering, 300 (2015), 99 – 106” have been attached in the appendix.

The Copyright and permission for reusing the context, figures, and tables of “F. Fan, J. Szpunar, The self-healing mechanism of an industrial acrylic elastomer. Journal of Applied Polymer Science, 132 (2015), 42135” have been attached in the appendix.