# Table of Contents

1. **Introduction** .................................................................................................................. 1  
   1.1 Background Information ............................................................................................... 1  
   1.2 Objectives and Significance of This Study ................................................................. 2  
   1.3 Organization of This Dissertation .............................................................................. 4  
   1.4 Reference .................................................................................................................... 6  

2. **Literature Review** ......................................................................................................... 8  
   2.1 Electrically Conductive Adhesives ............................................................................. 8  
      2.1.1 Polymer Binders and Conductive Fillers .............................................................. 9  
         2.1.1.1 *Polymer Binders for Electrically Conductive Adhesives* .............................. 9  
         2.1.1.2 Conductive Fillers ......................................................................................... 10  
      2.1.2 Conduction Mechanisms in Isotropic Conductive Adhesives ............................. 11  
      2.1.3 Cure Effects ......................................................................................................... 12  
      2.1.4 Review of Reliability Studies on Isotropic Conductive Adhesive (ICA) Joints ... 13  
   2.2 Theories of Adhesion .................................................................................................... 15  
      2.2.1 Adsorption ........................................................................................................... 15  
      2.2.2 Chemical Bonding ............................................................................................... 17  
      2.2.3 Mechanical Interlocking ....................................................................................... 17  
      2.2.4 Diffusion .............................................................................................................. 18  
      2.2.5 Electrostatic ......................................................................................................... 18  
   2.3 Water Adsorption and Diffusion in Polymer Systems ................................................. 19  
      2.3.1 Kinetics of Water Absorption and Water Distribution in Polymeric Materials ... 19  
      2.3.2 Effect of Water on the Adhesive .......................................................................... 21  
      2.3.3 Effect of Water on the Interface ......................................................................... 22  
   2.4 Fracture Testing ........................................................................................................... 23  
      2.4.1 Development of Fracture Mechanics .................................................................. 24  
      2.4.2 Double Cantilever Beam (DCB) Test .................................................................. 29  
   2.5 High Loading Rate Test .............................................................................................. 32
3. Environmental Aging Effects on Thermal and Mechanical Properties of Electrically Conductive Adhesives

3.1 Introduction

3.2 Experimental

3.2.1 Materials and Environmental Aging

3.2.2 Differential Scanning Calorimetry Analysis of ECAs

3.2.3 Moisture Uptake Measurements

3.2.4 Thermogravimetric Analysis of ECAs

3.2.5 Dynamic Mechanical Analysis of ECAs

3.2.6 Tensile Stress-Strain Testing

3.3 Results and Discussion

3.3.1 Properties of As-Cured Conductive Adhesives

3.3.1.1 DSC Results

3.3.1.2 TGA Results

3.3.1.3 DMA Results

3.3.1.4 Tensile Test Results

3.3.2 Effects of Environmental Aging on ECAs

3.3.2.1 Moisture uptake results

3.3.2.2 Effects of Environmental Aging on Thermal Stability of ECAs

3.3.2.3 Effects of Environmental Aging on Damping Behavior of ECAs

3.3.2.4 Effects of Environmental Aging on the Tensile Properties of ECAs

3.4 Summary and Conclusions

3.5 Reference

4. Environmental Aging Effects on the Durability of Electrically Conductive Adhesive Joints

4.1 Introduction

4.2 Experimental Procedure

4.2.1 Materials

4.2.2 Environmental Conditioning
4.2.3 Tensile Testing ................................................................. 94
4.2.4 Double Cantilever Beam (DCB) Testing .......................... 94
4.2.5 SEM and XPS Studies ......................................................... 95

4.3 Results and Discussion ...................................................... 96
4.3.1 Stress-Strain Results ......................................................... 96
4.3.2 DCB Results ................................................................ 96
4.3.3 Failure Mechanism of Conductive Adhesive Joints........... 100
  4.3.3.1 Copper-Plated Joints ..................................................... 100
  4.3.3.2 Gold-Plated Joints ......................................................... 103

4.4 Summary and Conclusions .................................................. 105
4.5 References ...................................................................... 106

5. Determining the Impact Resistance of Electrically Conductive Adhesives Using a Falling Wedge Test ................................................................. 130
5.1 Introduction .................................................................... 130
5.2 Experimental ................................................................. 133
  5.2.1 Materials ................................................................. 133
  5.2.2 Sample Preparation .................................................. 134
  5.2.3 Test Procedure ......................................................... 135
  5.2.4 Calculation of the Fracture Energy ............................. 136
5.3 Results and Discussions ..................................................... 138
  5.3.1 Falling Wedge Test Results .......................................... 138
  5.3.2 Relationship between Damping Properties and Impact Fracture Energy of the ECAs ......................................................... 140
  5.3.3 Correlation between Falling Wedge Test Results and Drop Test Results..... 143
5.4 Summary and Conclusions ................................................ 144
5.5 References ...................................................................... 145

6. Summary and Conclusions ..................................................... 164

Appendix A Formulations of ECA1, ECA2 and ECA3 Conductive Adhesives Provided by Emerson & Cumming ................................................................. 171
Appendix B  Mathematica File for Curve Fitting of Falling Wedge Test Results Based on Beam Theory .................................................................172
Appendix C  XPS Analysis on the Fracture Surfaces of Conductive Adhesive Joints 173
Appendix D  Effects of Environmental aging on Fracture Behavior of ECA Joints ...179
Appendix E  Modulus of ECA1, ECA2 and ECA3 as a Function of Aging Time.......183
Appendix F  Evaluation of the Long-Term Durability of High Performance Polyimide Adhesives and Their Bonds......................................................187
Vita..................................................................................................................212
List of Tables

Table 4.1 Fracture energy of aged and re-dried adhesive joints.................................111
Table 4.2 Atomic concentration on the fracture surfaces of the as-produced ECA2 bonded joint.................................................................112
Table 4.3 Atomic concentration on the fracture surfaces of the ECA2/Au bonded joint aged for 2 days. .................................................................113
Table 4.4 Atomic concentration on the metal side of fractured ECA1/Au, ECA2/Au and ECA3/Au joints aged for 50 days.........................................114
Table 5.1 The equivalent loss factor of the ECAs under impact test conditions........149
Table 5.2 Impact performance results of conductive adhesives.................................150
Table E.1 Tensile moduli of ECA1, ECA2 and ECA3 dogbone samples as a function of aging time at 85°C, 100%.........................................................183
Table F.1 DMA measurements of changes in Tg of FM-5 and PETI-5 resin samples following aging .................................................................198
Table F.2 Tensile stress-strain results on the first set of FM-5 neat resin samples as a function of aging time.........................................................199
Table F.3 Tensile stress-strain results on the second set of FM-5 and PETI-5 neat resin samples as a function of aging time.................................200
List of Figures

Figure 2.1 Conduction Mechanisms in conductive adhesives; (a) Particle-to-particle, (b) electron tunneling..........................12
Figure 2.2 DCB specimens with (a) load-blocks and (b) piano hinges..............30

Figure 3.1 Scanning electron micrograph of a conductive adhesive with silver flakes distributed in the epoxy matrix. ..................................................65
Figure 3.2 The TA Instruments Dynamic Mechanical Analyzer with a single cantilever clamp [35]................................................................66
Figure 3.3 Isothermal DSC scans at 150°C on ECA1, ECA2 and ECA3 adhesives ....67
Figure 3.4 DSC trace of as-cured ECA1 conductive adhesive sample................68
Figure 3.5 DSC trace of as-cured ECA2 conductive adhesive sample................69
Figure 3.6 DSC trace of as-cured ECA3 conductive adhesive sample...............70
Figure 3.7 TGA plots of as-cured electrically conductive adhesive samples.........71
Figure 3.8 Plots of tan δ of as-cured conductive adhesives obtained from DMA scans conducted at 1°C/min.............................................72
Figure 3.9 Typical stress-strain behavior of as-received ECA1, ECA2 and ECA3 samples tested at room temperature........................................73
Figure 3.10 Energy required to break ECA dogbone samples.........................74
Figure 3.11 Weight gain in ECA samples as a function of aging time, when exposed to at 85°C, 100% RH..............................................75
Figure 3.12 Differential thermogravimetric thermograms of as-cured and aged ECA1 samples heated at 10°C/min in nitrogen.........................76
Figure 3.13 Differential thermogravimetric thermograms of as-cured and aged ECA2 samples heated at 10°C/min in nitrogen............................77
Figure 3.14 Differential thermogravimetric thermograms of as-cured and aged ECA3 samples heated at 10°C/min in nitrogen............................78
Figure 3.15 Change of the loss factor of ECA1 as a function of aging time, as measured by DMA at 1Hz and 1°C/min...............................79
Figure 3.16  Effects of moisture on the damping properties of ECA1, as measured by DMA at 1Hz and 1°C/min. .................................................................80
Figure 3.17  The loss factor of aged and dried ECA1 samples, as measured by DMA at 1Hz and 1°C/min. .................................................................81
Figure 3.18  The loss factor of aged and dried ECA2 samples, as measured by DMA at 1Hz and 1°C/min. .................................................................82
Figure 3.19  The loss factor of aged and dried ECA3 samples, as measured by DMA at 1Hz and 1°C/min. .................................................................83
Figure 3.20  Failure stress of ECAs as a function of aging time. .........................84
Figure 3.21  Failure strain of ECAs as a function of aging time. .........................85
Figure 3.22  Typical stress-strain curves from aged and dried ECA1 samples. ............86
Figure 3.23  Typical stress-strain curves from aged and dried ECA2 samples. ............87
Figure 3.24  Typical stress-strain curves from aged and dried ECA3 samples. ............88
Figure 4.1  Typical stress-strain behavior of as-produced ECA1, ECA2 and ECA3 samples .........................................................................................114
Figure 4.1  Typical stress-strain behavior of as-produced ECA1, ECA2 and ECA3 samples .........................................................................................115
Figure 4.2  Fracture energy of ECA1–bonded DCB joints as a function of aging time. 116
Figure 4.3  Fracture energy of ECA2–bonded DCB joints as a function of aging time. 117
Figure 4.4  Fracture energy of ECA3-bonded DCB joints as a function of aging time...118
Figure 4.5  A three-phase diffusion model near the metal/polymer transition after [24].119
Figure 4.6  Fracture surface of ECA1 joints after 2 days aging with and without re-drying. .........................................................................................120
Figure 4.7  XPS spectra of the copper plated substrate prior to bonding (a) and the fractured bulk adhesive (b). .................................................................121
Figure 4.8  Micrographs of the fracture surfaces of the as-produced ECA2 bonded joint .........................................................................................122
Figure 4.9  Micrographs of the fracture surfaces of an as-produced ECA3 bonded joint123
Figure 4.10  XPS spectra of the fractured surface of ECA2/Cu joints aged for 2 days. (a) the substrate side; (b) the adhesive side. .................................124
Figure 4.11 XPS spectra of the fractured surface of ECA2/Cu joints aged for 50 days.
(a) the substrate side; (b) the adhesive side .................................................. 125

Figure 4.12 Cu 2p spectrum indicating the formation of CuO on the fracture surface of an ECA2/Cu joint .......................................................... 126

Figure 4.13 XPS spectra of the gold plated substrate prior to bonding .......................... 127

Figure 4.14 XPS spectra of the fractured surface of ECA2/Au joints aged for 2 days.
(a) the substrate side; (b) the adhesive side .................................................. 128

Figure 4.15 XPS spectra of the fractured surface of ECA2/Au joints aged for 50 days.
(a) the substrate side; (b) the adhesive side .................................................. 129

Figure 5.1 Schematic of Teflon spacer fabrication .................................................. 151

Figure 5.2 Sample fabrication configuration ..................................................... 152

Figure 5.3 Falling wedge test apparatus showing the drop tower arrangement and the high-speed digital camera from [15] ..................................................... 153

Figure 5.4 A photographic frame of a falling wedge test ..................................... 154

Figure 5.5 Fitting of experimental data with beam theory .................................... 155

Figure 5.6 Typical crack velocity versus time trace ........................................... 156

Figure 5.7 Typical fracture energy versus crack length trace ............................... 157

Figure 5.8 Typical plot showing the fracture energy versus crack velocity for ECA1 tested at room temperature ......................................................... 158

Figure 5.9 Summary of the falling wedge test results ........................................... 159

Figure 5.10 Micrographs of the fracture surfaces of ECA3 adhesive joints tested at (a) 60°C, and (b) -70°C ................................................................. 160

Figure 5.11 Changes of tan δ of conductive adhesives with temperature ................. 161

Figure 5.12 Correlation of the fracture energy and the loss factor obtained at 1 Hz ....... 162

Figure 5.13 Correlation of the fracture energy and the equivalent loss factor .......... 163

Figure C.1 XPS spectra of the fractured surface of ECA1/Cu joints aged for 50 days.
(a) the substrate side; (b) the adhesive side .................................................. 175

Figure C.2 XPS spectra of the fractured surfaces of ECA3/Cu joints aged for 50 days.
(a) the substrate side; (b) the adhesive side .................................................. 176

Figure C.3 XPS spectra of the fractured surfaces of ECA1/Au joints aged for 50 days.
(a) the substrate side; (b) the adhesive side .................................................. 177
Figure C. 4  XPS spectra of the fractured surfaces of ECA3/Au joints aged for 50 days.
(a) the substrate side; (b) the adhesive side .............................................178

Figure D. 1  Fracture energy of ECA1-bonded DCB joints as a function of aging time...180
Figure D. 2  Fracture energy of ECA2-bonded DCB joints as a function of aging time...181
Figure D. 3  Fracture energy of ECA3-bonded DCB joints as a function of aging time...182

Figure E. 1  Storage modulus of ECA1 samples as a function of aging time at 85°C,
100%. ...........................................................................................................184
Figure E. 2  Storage modulus of ECA2 samples as a function of aging time at 85°C,
100%. ...........................................................................................................185
Figure E. 3  Storage modulus of ECA3 samples as a function of aging time at 85°C,
100%. ...........................................................................................................186

Figure F. 1  DMA trace of a typical as-produced FM-5 sample .........................201
Figure F. 2  DMA trace of a typical FM-5 sample aged for 6 months in air at 204°C. ....202
Figure F. 3  DMA trace of a typical FM-5 sample aged for 30 months in air at 204°C. ..203
Figure F. 4  Failure stress and failure strain as a function of aging time for FM-5 resin
aged at 177°C in air .........................................................................................204
Figure F. 5  Failure stress and failure strain as a function of aging time for FM-5 resin
aged at 177°C in 2 psia ...................................................................................205
Figure F. 6  Failure stress and failure strain as a function of aging time for FM-5 resin
aged at 204°C in air .........................................................................................206
Figure F. 7  Schematics of DCB, ENF and MMF specimen geometries. (a) Symmetric
DCB, Pure Mode I; (b) End- notched flexure (ENF), Pure Mode II; (c)
Mixed-mode Flexure (MMF), 57% Mode I and 43% Mode II .......................207
Figure F. 8  DCB test results for different adhesive bonded systems ....................208
Figure F. 9  Strain energy release rate values under mode I, mode II and mixed mode
loading on the aliphatic sol-gel Ti/FM-5M adhesive bonded system ..........209
Figure F. 10 Static DCB test data on as-received and aged aliphatic sol-gel Ti/FM-5M
adhesive bonded joints .................................................................................210
Figure F. 11 Fractured surfaces of DCB specimens, both as-received and following
aging at 177°C and 204°C for 22 months ....................................................211