Title
Multifunctional composites: healing, heating and electromagnetic integration

Permalink
https://escholarship.org/uc/item/8889390p

Author
Plaisted, Thomas Anthony John

Publication Date
2007

Peer reviewed|Thesis/dissertation
MULTIFUNCTIONAL COMPOSITES: HEALING, HEATING AND ELECTROMAGNETIC INTEGRATION

A Dissertation submitted for partial satisfaction of the requirements for the degree

Doctor of Philosophy

in

Materials Science and Engineering

by

Thomas Anthony John Plaisted

Committee in charge:

Professor Sia Nemat-Nasser, Chair
Professor Prabhakar Bandaru
Professor Vistasp Karbhari
Professor Lea Rudee
Professor Yitzhak Tor

2007
The Dissertation of Thomas Anthony John Plaisted is approved and it is acceptable in quality and form for publication on microfilm:

Chair

University of California, San Diego

2007
DEDICATION

To my parents, whose love of learning was a great inspiration in the pursuit of this degree, and to my wife, April, and baby, Lucy, for bearing with me through all of it. Your love and support have made everything possible.
TABLE OF CONTENTS

SIGNATURE PAGE .................................................................................................................... iii

DEDICATION ................................................................................................................................ iv

TABLE OF CONTENTS ............................................................................................................... v

LIST OF FIGURES .................................................................................................................. ix

LIST OF TABLES .................................................................................................................... xx

ACKNOWLEDGEMENT ........................................................................................................... xxi

VITA and PUBLICATIONS .................................................................................................... xxiv

ABSTRACT OF THE DISSERTATION .................................................................................... xxvii

1 Introduction .......................................................................................................................... 1

1.1 Organization of Chapters ............................................................................................... 3

2 Electromagnetically Functional Structural Composites ....................................................... 5

2.1 Electromagnetic Functionality ....................................................................................... 5

2.2 Thin Wire Plasmon Media Composites ........................................................................ 6

2.3 Electromagnetic Simulation and Characterization ....................................................... 7

2.4 Integration into Composites .......................................................................................... 11

2.5 Coiled Wire Plasmon Media Composites .................................................................... 18

2.6 Heating Functionality .................................................................................................. 29

2.7 Acknowledgement ........................................................................................................ 31

3 Crack Healing in Polymers ............................................................................................... 33

3.1 Polymer Background .................................................................................................... 33
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>Crack Healing in Thermoplastic Polymers</td>
<td>35</td>
</tr>
<tr>
<td>3.3</td>
<td>Crack Healing in Thermoplastic Composites</td>
<td>37</td>
</tr>
<tr>
<td>3.4</td>
<td>Crack Healing in Cross-linked Polymers and Polymer Composites</td>
<td>43</td>
</tr>
<tr>
<td>3.5</td>
<td>Autonomic Healing Fibers in Fibrous Composites</td>
<td>53</td>
</tr>
<tr>
<td>3.6</td>
<td>Discussion of the Composite Healing Systems</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>Thermally-reversible Cross-linking Polymer</td>
<td>58</td>
</tr>
<tr>
<td>4.1</td>
<td>Diels-Alder Cycloaddition</td>
<td>58</td>
</tr>
<tr>
<td>4.2</td>
<td>3M4F Polymer</td>
<td>59</td>
</tr>
<tr>
<td>4.3</td>
<td>2MEP4F Polymer</td>
<td>66</td>
</tr>
<tr>
<td>4.4</td>
<td>Summary of the Diels-Alder Polymer</td>
<td>72</td>
</tr>
<tr>
<td>4.5</td>
<td>Acknowledgement</td>
<td>73</td>
</tr>
<tr>
<td>5</td>
<td>Mechanical, Thermal, Electromagnetic and Other Measurements of 3M4F and 2MEP4F Polymers</td>
<td>74</td>
</tr>
<tr>
<td>5.1</td>
<td>Preliminary DCDC Testing</td>
<td>74</td>
</tr>
<tr>
<td>5.2</td>
<td>Compression Testing</td>
<td>76</td>
</tr>
<tr>
<td>5.3</td>
<td>Thermal Analysis</td>
<td>78</td>
</tr>
<tr>
<td>5.4</td>
<td>Interfacial Shear Strength</td>
<td>92</td>
</tr>
<tr>
<td>5.5</td>
<td>Viscosity Determination</td>
<td>93</td>
</tr>
<tr>
<td>5.6</td>
<td>Dielectric Measurement of Polymer 3M4F</td>
<td>97</td>
</tr>
<tr>
<td>5.7</td>
<td>Polymer 2MDPM 4F</td>
<td>100</td>
</tr>
<tr>
<td>5.8</td>
<td>Acknowledgement</td>
<td>101</td>
</tr>
<tr>
<td>6</td>
<td>Experimental Technique for the Measurement of Fracture and Repair of Healable Polymers</td>
<td>102</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1-1. Illustration of the many integrated functions within the human skin.................................................................................................................................2

Figure 2-1. Anachoiric chamber at UCSD Physics Department for EM characterization. .................................................................................................................. 10

Figure 2-2. [Top] Schematic (courtesy A. Starr) and [bottom] photo of Focused Beam system for EM characterization from 5-40GHz at UCSD's CEAM.................................................. 11

Figure 2-3. [Top] Schematic of two dimensional thin wire array. [Bottom] Laminating hot presses for processing composite panels......................... 15

Figure 2-4. Numerical and experimental characterization of the samples listed in Table 2-1. (A) 50µm (0.002”) diameter wires embedded in Cyanate Ester/Quartz composite. (B) 50µm diameter wires embedded in Vinyl Ester/Spectra composite.............................................. 16

Figure 2-5. (C) 75µm (0.003”) diameter wires embedded in Epoxy/E-glass composite. (D) 50µm diameter wires embedded in Epoxy/E-glass composite................................................................. 17

Figure 2-6 [Top Left] Schematic of tubular braiding machine.  [Top Right] Arrow indicates path taken by one yarn carrier in maypole braiding pattern. [Bottom] Photograph of tubular braiding machine at CEAM................................................................. 20

Figure 2-7. Concept drawing of fibrous braid encasing functional elements (red) such as a sensor (courtesy A. Starr).................................................. 21
Figure 2-8. [Top] Schematic of braid cross-section consisting of tows of Kevlar fibers, nylon fibers, and copper wire. [Center] Schematic of outside of braided architecture with 2 up 2 down braid pattern [Bottom] Photograph of braids bi-directionally woven into fabric. ..........24

Figure 2-9. [Top] Test frame containing Kevlar braided with copper wire. Braids are arranged such that adjacent braid elements contain wire coils with opposite sense (inset). [Bottom] Simulated (dashed line) and experimental (circles) characterization of the braided elements...........26

Figure 2-10. [Top left] Coiled wire architecture integrated with structural Kevlar fibers by braiding. Braids are woven [top right] into fabric [lower left] and laminated into composite plates [bottom right] by hot press. .......................................................................................................27

Figure 2-11. EM characterization of the braided/woven composite showing typical plasmon media response when aligned parallel to the direction of EM radiation. Normal (non-plasma) dielectric response is observed when aligned perpendicular......................................................28

Figure 2-12. Wiring arrangement for resistively heated composite panel consisted of twelve wire sets connected in series, where each wire set contained 4 copper wires connected in parallel (Santos et al. 2004). .................................................................30

Figure 2-13. Heating curve for 100µm diameter copper wire array embedded in a glass fiber/epoxy composite. The panel was insulated and heated at a power density of 0.073 W/cm² (Santos et al. 2004). ...............30

Figure 2-14. Heating curve for 100µm diameter copper wire array embedded in a glass fiber/epoxy composite. The panel was not insulated and heated at a power density of 0.200 W/cm² (Santos et al. 2004).. ...............31
Figure 3-1. Crack healing experiments by on PMMA. Stress intensity vs. time from Wool and O'Connor (1981a)............................................................... 37

Figure 3-2. Lap shear strength of welded PEEK compared to epoxy adhesive joints (Cantwell et al. 1989).........................................................................40

Figure 3-3. Healing of PEEK/carbon fiber composite at high temperature (Davies et al. 1989)......................................................................................40

Figure 3-4. Healing of PEEK/carbon fiber composite over short times (Davies et al. 1989). ..................................................................................................40

Figure 3-5. SEM micrographs of PEEK composite interfaces after healing. (a) and (b) Short time/ lower temperature resulted in poor contact and interdiffusion. (c) Longer time/ higher temperature produced optimal weld (Davies et al. 1989)........................................................................ 41

Figure 3-6. Healing concept of autonomic healing polymer (White et al. 2001).............................................................................................................46

Figure 3-7. Design of microcapsule to attract the propagating crack (White et al. 2001)............................................................................................................46

Figure 3-8. SEM micrograph of fractured microsphere (White et al. 2001)......... 47

Figure 3-9. Reaction system of the autonomic healing composite (White et al. 2001).............................................................................................................47

Figure 3-10. Loading curve showing ~70% healing efficiency (White et al. 2001).............................................................................................................47

Figure 3-11. Effect of microcapsule loading and size on fracture toughness (Brown et al. 2004).......................................................................................48
Figure 3-12. The three testing schemes for the autonomic healing composite.

Composite panel is: (a) Injected and catalyzed. (b) Injected and self-catalyzing. (c) Fully self-healing (Kessler et al. 2003)..............................52

Figure 3-13. Representative loading curves for the virgin and the autonomically healed composite samples. On average 38% of the original fracture load was recovered (Kessler et al. 2003) .........................52

Figure 3-14. SEM micrograph of the fracture surface of a self-healing specimen. (Kessler et al. 2003)............................................................52

Figure 3-15. Illustration of various hollow fiber self-healing systems (Bleay et al. 2001).................................................................................54

Figure 3-16. Distribution of hollow fibers filled with healing agents within the composite (Trask and Bond 2006)..................................................54

Figure 4-1. Diels-Alder cycloaddition of butadiene and ethane..........................58

Figure 4-2. [Top] Tetrafuran molecule and [middle] trimaleimide molecule polymerize to form [bottom] DA cycloadduct. .................................60

Figure 4-3. Degree of polymerization vs. time at various temperatures. Open square polymerized at 24°C; closed down arrow at 45°C; open up arrow at 75°C (Chen et al. 2002). .........................................................62

Figure 4-4. Degree of polymerization after various thermal cycling. (Chen et al. 2002)..................................................................................62

Figure 4-5. Solid state C-NMR. [Top] Resonance values for the furan moiety and furan maleimide adduct. (Chen et al. 2002)..............................63

Figure 4-6. (A) Typical loading curve of the virgin polymer versus the healed polymer. Optical micrographs of the fractured (B) and healed (C)
samples. (D) SEM micrograph of the scar surface. (E) magnification of (D) (Chen et al. 2002). .....................................................65

Figure 4-7. Previous reaction scheme for tetracarboxylic compound. .........................67

Figure 4-8. Revised reaction scheme for tetracarboxylic compound improves reaction efficiency. ..........................................................67

Figure 4-9. Reaction of tetracarboxylic compound into tetrafuran. .........................68

Figure 4-10. Synthesis of 2MEP bismaleimide compound. ........................................69

Figure 4-11. Solid state C-NMR testing of 2MEP 4F polymer, with similar results to Figure 4-5 (Chen et al. 2003). ..................................................70

Figure 4-12. Left – Compact tension geometry showing location of crack arresting hole. Right - Typical loading curve for compact tension testing of virgin and healed 2MEP4F polymer showing recovery of 81% of fracture load (Chen et al. 2003). ..................................................72

Figure 5-1. [Top] – Schematic of miniature DCDC geometry used in preliminary testing. [Middle] - Diagonal view of optical photograph taken at 20X magnification of representative 3M4F sample after cracking. [Bottom] - Sample after healing. ......................................................75

Figure 5-2. Schematic of classical compression split Hopkinson bar technique for high strain rate testing.................................................................76

Figure 5-3. Compression testing of 3M4F and 2MEP4F polymers. [Top] High strain rate testing at 2000 sec\(^{-1}\). [Bottom] Low strain rate testing at 0.001 sec\(^{-1}\). .....................................................................................77

Figure 5-4. Temperature modulated DSC of polymer 2MEP4F. ...............................80
Figure 5-5. Results of Differential Scanning Calorimetry on 2MEP4F polymer.

Figure 5-6. DSC scan of reversing and non-reversing heat flows of 2MEP4F polymer and carbon composite with 2MEP4F polymer.

Figure 5-7. DSC scan of reversing and non-reversing heat flows of 2MEP4F polymer and S-2 glass composite with 2MEP4F polymer.

Figure 5-8. DSC scan of 2MEP bismaleimide monomer.

Figure 5-9. DSC scan of 4F furan monomer.

Figure 5-10. DSC scans of furan and bismaleimide monomers relative to the 2MEP4F polymer.

Figure 5-11. DSC scan of 2MEP4F polymer, carbon fiber, and composite fabricated from these two components.

Figure 5-12. Diagram of cantilever bending grips for DMTA (TA Instruments 2002).

Figure 5-13. DMTA of neat 2MEP4F polymer.

Figure 5-14. DMTA of 2MEP4F (Chen 2003).

Figure 5-15. DMTA of 2MEP4F/carbon composite.

Figure 5-16. CTE measurement of polymer 2MEP4F.

Figure 5-17. Schematic [left] of microbond apparatus [right] to measure interfacial shear strength of 2MEP4F polymer with composite fibers.

Figure 5-18. Viscosity measurements for 4F furan and 2MEP bismaleimide monomers.
Figure 5-19. Schematic of cone and plate viscometer ................................................. 96

Figure 5-20. Gordon Coupler and network analyzer for measuring dielectric properties. ........................................................................................................ 97

Figure 5-21. Shift in resonant frequency of TE 101 cavity when loaded with 3M4F sample. ........................................................................................................ 99

Figure 5-22. Simulated frequency vs. dielectric constant for mode 1 resonance in TE 101 cavity.......................................................................................... 99

Figure 5-23. Structure of 2MDPM monomer............................................................ 101

Figure 6-1. DCDC specimen with central hole. Solid lines emanating from the crowns of the hole indicate the shape and location of the initial pre-cracks. Upon loading, pre-cracks connect and propagate (dotted lines) towards the direction of applied compression. ................................... 106

Figure 6-2. Picture sequence, from left to right, top to bottom, of advancing crack. The lower left shows the sample loaded well into the plateau regime. Sample is viewed from same perspective as shown in Figure 6-1 ................................................................. 112

Figure 6-3. Experimental data for specimens with w/R ratios 2 and 4. ................. 114

Figure 6-4. Experimental data for specimens with w/R ratios 3 and 5............... 115

Figure 6-5. Stress distribution during crack propagation in PMMA specimen under increasing axial compression (left to right, top to bottom)............. 118

Figure 6-6. Stress distribution during crack propagation in PMMA specimen. Photos taken with no axial compression applied to specimen............... 119
Figure 6-7. Model for DCDC specimen with \( w/R \) ratio of 3. The end of the
stable crack growth occurs roughly when the crack has reached
length equivalent to the radius of the hole (\( \lambda \approx 1 \)).

Figure 6-8. Representation of a slit crack with symmetric concentrated loads.

Figure 6-9. Schematics and dimensions of the DCDC model.

Figure 6-10. Normalized values of \( d(w/R) \) with respect to the theoretical
prediction in an infinite plate.

Figure 6-11. Plateau stress versus \( w/R \) ratio. The solid curve represents the
model result for a critical stress intensity factor of
\[ K_{IC} = 0.71 \text{MPa}\sqrt{m}, \]
while the dashed curves are for a 10%
variation, i.e., \( K_{IC} = 0.64, 0.78 \text{MPa}\sqrt{m}. \)

Figure 6-12. Axial load versus normalized crack length for \( w/R=2 \) and 4: The
solid and dashed curves represent the model results for the indicated
values of \( w/R \), using the critical stress intensity factors
\[ K_{IC} = 0.71 \text{MPa}\sqrt{m} \text{ and } K_{IC} = 0.64, 0.78 \text{MPa}\sqrt{m}. \]

Figure 6-13. Axial load versus normalized crack length for \( w/R=3 \) and 5: The
solid and dashed curves represent the model results for the indicated
values of \( w/R \), using the critical stress intensity factors
\[ K_{IC} = 0.71 \text{MPa}\sqrt{m} \text{ and } K_{IC} = 0.64, 0.78 \text{MPa}\sqrt{m}. \]

Figure 7-1. The healable polymer consists of a multifuran molecule combined
in stoichiometric ratio with a multimaleimide molecule to form
2MEP4F cycloadduct.

Figure 7-2. Dynamic Mechanical Analysis of 2MEP4F polymer cycled at 1Hz
and heated at 3°C/min.
Figure 7-3. Lateral confining fixture attached to specimen to create pre-crack.  
...................................................................................................................146

Figure 7-4. Top - Schematic of DCDC sample geometry. Bottom - Fracture  
and healing sequence of a single sample. ..................................................149

Figure 7-5. Stress vs. crack length data of 5 fracture-healing cycles for  
specimen 1. ...............................................................................................154

Figure 7-6. Initial portion of stress vs. crack length data shown in Figure 7-5  
for specimen 1............................................................................................155

Figure 7-7. Effect of different healing treatments on the resulting fracture  
strength of specimen 2. ............................................................................158

Figure 7-8. Initial portion of stress vs. crack length data shown in Figure 7-7  
for specimen 2............................................................................................159

Figure 7-9. Fracture and healing on specimen 3. ......................................................161

Figure 7-10. Initial portion of stress vs. crack length data shown in Figure 7-9  
for specimen 3............................................................................................162

Figure 7-11. Fracture into virgin polymer for specimen 4 in relation to model  
prediction with $K_c = 0.692 \text{ MPa\cdot m}^{1/2}$, and specimen 4 after 5 cycles  
of fracturing and healing with $K_c = 0.716 \text{ MPa\cdot m}^{1/2}$..................166

Figure 7-12. Illustration of in-situ photos of representative healing treatment at  
85°C. Sequence of photos during treatment at 85°C. (A) Time 0.  
(B) 2 minutes (C) 4 minutes (D) 15 minutes. .............................................169

Figure 7-13. Fracture and healing of specimen 5 with $w/R$ ratio of 3. Poor  
healing efficiency observed when the virgin crack length is extended  
into the plateau regime.............................................................................173
Figure 7-14. Specimen 6 with w/R ratio of 3. Near complete healing efficiency is observed when virgin crack length is kept below the plateau region................................................................. 174

Figure 7-15. Fracture and healing sequence of a specimen 6. A) Virgin sample with hole and pre-cracks visible; B) Sample after first fracture event; C) Sample after first healing treatment; D) Sample after second fracture event........................................................................ 175

Figure 8-1. The polymer consists of a multifuran molecule combined in stoichiometric ratio with a multimaleimide molecule to form 2MEP4F cycloadduct........................................................................ 180

Figure 8-2. SRIM apparatus (upper left and right) was developed for injection of self-healing liquid monomers (lower left) into fiber preform (lower right). ................................................................. 182

Figure 8-3. Single cantilever beam of [90/0]s laminate tested using Dynamic Mechanical Thermal Analysis to quantify microcracking and subsequent healing of healable composite................................. 184

Figure 8-4. A. Composite is fabricated in a [90 / 0 / 0 / 90] layup. Single cantilever beam (B) measurement of storage modulus is used to characterize virgin/cracked/healed states of the composite.................. 187

Figure 8-5. Average storage modulus and standard deviation of three measurements for glass composite sample 1 after microcracking and thermal healing treatments....................................................... 189

Figure 8-6. Average storage modulus and standard deviation of three measurements for glass composite sample 2 after microcracking and thermal healing treatments....................................................... 190
Figure 8-7. Storage modulus and tan delta for carbon composite sample 2 during cooling from 30 to -120°C. ............................................................192

Figure 8-8. Average storage modulus and standard deviation of three measurements for carbon composite sample 1 after microcracking and thermal healing treatments. ........................................................................194

Figure 8-9. Average storage modulus and standard deviation of three measurements for carbon composite sample 2 after microcracking and thermal healing treatments. ............................................................195

Figure 8-10. Micrographs at 400x of carbon composite sample 2 of crack that did not heal. Crack visible before (top) and after (bottom) healing treatment at 95°C. ...............................................................................................196

Figure 8-11. Micrographs at 400x of carbon composite sample 2 of microcracks that healed. Microcrack visible after cryogenic cycling (top) and healing of those cracks after treatment at 95°C (bottom). .......197

Figure 8-12. Storage modulus and tan delta for carbon composite during heating from 35°C to 135°C. ....................................................................................................................198

Figure 9-1. Lap shear joint with typical crack initiation at stress concentration within adhesive fillet zone. These critical locations are where a self-healing polymer will be most effective at repairing damage before catastrophic failure occurs. ......................................................................................206

Figure 9-2. Expand current DCDC testing to include measurement of fracture resistance of bimaterial interface. .....................................................................................................................207
LIST OF TABLES

Table 2-1. Description of representative fiber reinforced composite panels made at CEAM. Composite Materials – Epoxy glass (EG), cyanate ester quartz (CEQ), and vinyl ester Spectra (VES). ........................................... 13

Table 6-1. Specimen dimensions ........................................................................................................... 108

Table 7-1. Specimen dimensions ........................................................................................................... 145

Table 7-2. Healing efficiency of Specimen 1 ...................................................................................... 156

Table 7-3. Efficiency of different healing procedures for specimen 2 ............................................ 160

Table 7-4. Healing efficiency of specimen 3 ......................................................................................... 163

Table 8-1. Healing efficiency (storage modulus with respect to virgin storage modulus) after cryogenic cycling and thermal healing treatments for glass composite sample 1 .............................................................................. 189

Table 8-2. Healing efficiency after cryogenic cycling and thermal healing treatments for glass composite sample 2. ........................................................ 190

Table 8-3. Healing efficiency after cryogenic cycling and thermal healing treatments for carbon composite sample 1. ............................................................ 194

Table 8-4. Healing efficiency after cryogenic cycling and thermal healing treatments for carbon composite sample 2. ............................................................ 195
ACKNOWLEDGEMENT

Foremost, I thank my advisor, Professor Sia Nemat-Nasser, for his guidance and support in pursuing this research. I have been inspired by his dedication to teaching and the numerous contributions he continues to make in many diverse fields of science. I also thank the members of my committee: Professor Prabhakar Bandaru, Professor Vistasp Karbhari, Professor Lea Rudee and Professor Yitzhak Tor, for their valuable input towards helping me complete this dissertation.

I would like to thank all with whom I have worked at the Center of Excellence for Advanced Materials over the course of my research. In particular, I thank Jon Isaacs for contributing his keen intuition for all things mechanical, which was essential in designing experiments to glean the most useful information from limited supplies of material. I thank Benjamin Cook for assistance in the design of the injection molding device used in fabricating the healable composite, in addition to the many technical and non-technical discussions we had in the lab. I thank Alireza Vakil Amirkhizi for his contributions to the electromagnetic modeling described in this dissertation, as well as for his contributions to the development of the mathematical model for crack propagation in the DCDC geometry. I also thank Tony Starr, Syrus Nemat-Nasser, Jack Mock and Diego Arbelaez for their contributions to the theoretical and experimental aspects of the electromagnetic work. For contributions to the heating functionality reported here, I thank Carlo Santos. I greatly appreciate working with Jon Isaacs, Ben Cook, David Lischer, Fabrizia Ghezzo, Diego Arbelaez, Dirk Van Ulden and Phillip Little in carrying out these and many other experiments within the
labs at CEAM. And I thank Lauri Jacobs for tirelessly attending to the administrative
details of my studies while at UCSD.

I am indebted to Professor Fred Wudl, Dr. Xiangxu Chen, and Dr. Sunny
Skaria of the UCLA Exotic Materials Institute for sharing their expertise on the
synthesis of the healable polymers. I also am grateful to the Campus Research
Machine Shop at UCSD, in particular Gary Foreman, for expertly machining the
numerous fixtures and samples used in the measurements throughout this dissertation.
Despite breaking many of these parts, some on purpose and others not, I am glad to
say that those which could be healed were brought back to their original state and live
on today.

And finally, I thank my wife and daughter for their love and patience
throughout the writing of this dissertation. Now that it is complete, I promise to fix
the plumbing.

Chapter 2 includes content which has appeared in “Chapter 12: Multifunctional
Press. The dissertation author was the primary author and investigator of this work.
Chapter 6 describes experimental and theoretical results which have appeared in
“Compression-induced Axial Crack Propagation in DCDC Polymer Samples:
Amirkhizi, A. V.; and Nemat-Nasser, S., published by Springer. The dissertation author was the primary author and investigator on this work. Chapter 7 contains experimental work which is to appear in “Quantitative Evaluation of Fracture, Healing and Re-healing of a Reversibly Cross-linked Polymer”, *Acta Materialia*, 2007, Plaisted T.; and Nemat-Nasser S., published by Elsevier. The dissertation author was the primary author and investigator on this work.

This work has been supported by DARPA (Dr. Leo Christodoulou's Synthetic Multifunctional Materials Program) through ARO DAAD19-00-1-0525 contract to the University of California, San Diego.
VITA and PUBLICATIONS

1998-2000 Undergraduate Research Assistant, Department of Materials Science and Engineering, University of Kentucky

2000 Bachelor of Science in Materials Science and Engineering, University of Kentucky

2001 Master of Science in Materials Science and Engineering, University of California, San Diego

2000-2006 Graduate Research Assistant, Center of Excellence for Advanced Materials, University of California, San Diego

2006-Present Senior Research Engineer, Luna Innovations Incorporated, Blacksburg, Virginia

2007 Doctor of Philosophy in Materials Science and Engineering, University of California, San Diego

BOOK CHAPTER


ARCHIVAL JOURNALS


**REVIEWED PROCEEDINGS**


**OTHER PROCEEDINGS**


Multifunctional materials, in the context of this research, integrate other functions into materials that foremost have outstanding structural integrity. Details of the integration of electromagnetic, heating, and healing functionalities into fiber-reinforced polymer composites are presented. As a result of fiber/wire integration through textile braiding and weaving, the dielectric constant of a composite may be tuned from negative to positive values. These wires are further leveraged to uniformly heat the composite through resistive heating. A healing functionality is introduced by
utilizing a polymer matrix with the ability to heal internal cracking through thermally-reversible covalent bonds based on Diels-Alder cycloaddition.

The Double Cleavage Drilled Compression (DCDC) specimen is applied to study the fracture and healing characteristics of the neat polymer. This method allows for quantitative evaluation of incremental crack growth, and ensures that that the cracked sample remains in one piece after the test, improving the ability to re-align the fracture surfaces prior to healing. Initially, the fracture strength of PMMA is studied with various DCDC geometries to develop a model of the propagation of a crack within this type of specimen. Applied to the healable polymer (2MEP4F), repeated fracture-healing cycles demonstrate that treatment at temperatures between 85 to 95°C results in full fracture toughness recovery and no dimensional changes due to creep. The fracture toughness after each fracturing and healing cycle has been calculated, using the model, to yield a fracture toughness of about 0.71 MPa·m$^{1/2}$ for this material at room temperature.

Glass and carbon fiber-reinforced composites have been fabricated with the 2MEP4F polymer, and the ability of this polymer to heal microcracks in fiber-reinforced composites is demonstrated. Microcracks have been introduced into the composites by cryogenic cycling in liquid nitrogen, causing a reduction in the storage modulus of the composites as measured by Dynamic Mechanical Thermal Analysis (DMTA). Heating the laminate with pressure applied normal to transverse microcracks appeared to repair the cracks and partially recover of the composite's
stiffness. Multifunctional composites with such unique capabilities have tremendous potential to impact future structural applications.
1 Introduction

Multifunctional structural materials possess attributes beyond the basic strength and stiffness that typically drive the science and engineering of the materials for structural systems. The materials can be designed to have integrated electrical, magnetic, optical, locomotive, power generative, and possibly other functionalities that work in synergy to provide advantages that reach beyond that of the sum of the individual capabilities. Materials of this kind have tremendous potential to impact future structural performance by reducing size, weight, cost, power consumption and complexity while improving efficiency, safety, and versatility.

Nature offers numerous examples of materials that serve multiple functions. Biological materials routinely contain sensing, healing, actuation, and other functions built into the primary structures of an organism. The human skin, for instance (see Figure 1-1), consists of many layers of cells, each of which contains oil and perspiration glands, sensory receptors, hair follicles, blood vessels, and other components with functions other than providing the basic structure and protection for the internal organs. These composite structures have evolved in nature over eons to the level of seamless integration and perfection with which they serve their functions. Scientists now seek to mimic these material systems in designing synthetic multifunctional materials using physics, chemistry, and mathematics to their advantage in competing with the unlimited time frame of nature’s evolutionary design process. The multifunctionality of these materials often occurs at length scales from the nano- through macro-scales and on various spatial and compositional levels.
Another characteristic of the human skin is its remarkable ability to heal. Nature has long demonstrated this property in various biological materials, whereas, until recently, synthetic self-healing materials had not been developed. However, interest in synthetic self-healing materials has recently gained significant attention with the creation of a truly autonomic healing polymer by White and other researchers at the University of Illinois (White et al. 2001). Research in this area has since grown significantly as demonstrated by special journal issues dedicated to the topic\(^1\) as well as new conferences like the 1\(^{st}\) International Conference on Self-Healing Materials.\(^2\) Other novel materials have been proposed, one of which is a novel polymer based on reversible covalent cross-linking (Chen et al. 2002). Mechanical failure of this

---

polymer occurs preferentially along these cross-links, and due to the reversible nature of this bond, it may be repaired by application of moderate heat.

1.1 Organization of Chapters

This dissertation is composed of individual chapters that describe the integration and characterization of novel functionalities into polymer composite materials. Chapter 2 describes the incorporation of plasmon media into fiber reinforced polymers to tune the electromagnetic characteristics of the material. A further consequence is the introduction of a heating functionality within the material. This work has appeared in “Chapter 12: Multifunctional Materials”, *Biomimetics: Biologically Inspired Technologies*, Nemat-Nasser, S.; Nemat-Nasser, S. C.; Plaisted, T.; Starr, A.; and Amirkhizi, A. V., published by CRC Press. Chapter 3 provides a review of healing in polymers and polymer composites, including a description of healing in thermoplastics and autonomic healing systems, while Chapter 4 describes the pioneering research on a reversible covalently cross-linked polymer, which is the focus of much of the work in the remaining chapters. Chapter 5 details a variety of mechanical, thermal, electromagnetic, and other properties of this polymer measured by the dissertation author. Chapter 6 describes the application of a novel method to introduce controlled fracture into polymer specimens and the development of a model to describe the fracture propagation. Portion of this work appeared in “Compression-induced Axial Crack Propagation in DCDC Polymer Samples: Experiments and Modeling”, *International Journal of Fracture*, 2006, Plaisted, T. A.; Amirkhizi, A. V.; and Nemat-Nasser, S., published by Springer. In Chapter 7, this method and model
are applied to study the healing efficiency of the reversible, covalently cross-linked polymer. This work is to appear in “Quantitative Evaluation of Fracture, Healing and Re-healing of a Reversibly Cross-linked Polymer”, *Acta Materialia*, 2007, Plaisted T.; and Nemat-Nasser S., published by Elsevier. Chapter 8 describes the integration of the healing functionality of this polymer into a fiber-reinforced composite, and Chapter 9 provides a conclusion and areas of future research to build upon this work. Due to the standalone nature of these chapters, some information is repeated for clarity.
2 Electromagnetically Functional Structural Composites

Recent advances in electromagnetics have yielded methods of changing the dielectric constant, as well as the index of refraction, from negative through positive values. These functions have been integrated into traditional laminated polymer composites through various techniques. As a further consequence, a method of controlling the thermal properties of the material has resulted.

2.1 Electromagnetic Functionality

As an example of increasing the functionality of structural composite materials, electromagnetic (EM) enhancements may be introduced in the form of a tunable index of refraction, radio frequency (RF) absorption, and when considering Negative Index Materials, a negative index of refraction (Smith et al. 2000). Such properties are the result of embedding periodic metal scattering elements into the material to create an effective medium response over desired RF frequency ranges.

Based on initial work by Pendry et al. (1998) and Smith et al.(1999), two wire architectures have been identified, namely thin straight wire arrays and coiled wire arrays, that are suitable for direct integration into fiber-reinforced composites (Nemat-Nasser et al. 2002). These arrays act as inductive structures with a plasma-like response to control the electric permittivity. As a result, the dielectric constant may be tuned to negative or positive values. Such a medium may be used as a filter of electromagnetic radiation. When the dielectric constant is negative the material does not transmit incident radiation. As the dielectric constant approaches the turn-on...
frequency, its dielectric constant becomes positive and EM radiation is transmitted. Furthermore, over a desired frequency range the dielectric constant may be tuned to match that of the surrounding environment. For instance the dielectric constant may be tuned to match that of air, with a dielectric constant of one, such that incident radiation does not perceive the difference.

### 2.2 Thin Wire Plasmon Media Composites

Introduction of structured thin conductive wires into any dielectric medium creates plasmonic effects that modify the overall electromagnetic material properties of the medium. In principle, a plasma is defined as a medium in which freely moving charges are abundant. The dielectric constant $\kappa$ of a dilute plasma can be written as:

$$
\kappa = 1 - \left( \frac{f_p}{f} \right)^2
$$

Equation 2-1

where $f_p$ is the plasma frequency and $f$ is the electromagnetic excitation frequency. This parameter must be evaluated empirically for any configuration, but analytical and numerical results can be easily used for design purposes. Pendry et al. (1996) provide the following analytical formula for thin wire media:

$$
f_p = \frac{c_0}{d} \sqrt{\frac{1}{2\pi(\ln\left(\frac{d}{r}\right) - \frac{1}{2}(1 + \ln \pi))}}
$$

Equation 2-2

where $c_0$ denotes the speed of light in vacuum, $d$ is the lattice spacing, and $r$ is the radius of the wires. Straight wire arrays, such as those shown in Figure 2-3, are
designed such that the radius of the wires is very small compared to the lattice spacing, so that the wavelength of the electromagnetic excitation frequency is large compared to the lattice size. For the medium to behave as a plasma at microwave frequencies, for instance, the wire radius must be on the order of tens of micron and spaced on the order of centimeters.

2.3 Electromagnetic Simulation and Characterization

Frequency domain calculations may be performed to predict the EM response of the medium. The HFSS electromagnetic finite element calculation package\(^3\) was used to predict the dispersion relation of a periodic medium. Initially a cubic unit cell must be created that, when repeated in three directions, spans the entire medium. If an electromagnetic wave is propagating in the \(x\) direction, the faces of the unit cell parallel to this direction will have the same field values and the field solutions in \(y\) and \(z\) directions are periodic. The fields on the other two faces normal to the direction of propagation have a phase shift \(\varphi\) relative to each other. The shift can be written in terms of the wavelength as:

\[ \varphi = \frac{2\pi d}{\lambda} \]

Equation 2-3

where \(d\) represents the size of the unit cell in the propagation direction and \(\lambda\) is the wavelength. The unit cell is created in the software and appropriate material properties are assigned. The boundary conditions are set to be periodic on the faces normal to the \(y\) and \(z\) directions and periodic with phase advance parameter \(\varphi\) on the faces normal to

\(^3\) ANSOFT Corp.
the $x$ direction. The resonance frequency of such a configuration is the frequency of the propagating wave through the periodic medium with wavelength $\lambda$. For example, the resonant frequency when $\varphi = 0^\circ$ is the smallest possible frequency of a propagating electromagnetic wave, referred to as the turn-on frequency of the medium. Below the turn-on the medium exhibits a stop band behavior. The index of refraction of such a medium will be frequency dependent and can be written as:

$$n = \frac{\varphi \varepsilon_0}{2\pi f d},$$  \hspace{1cm} \text{Equation 2-4}$$

It should be mentioned here that based on analytical and experimental results, the magnetic activity from the thin wire medium is very low. Therefore the effective real part of the dielectric constant of the medium may be approximated as:

$$\varepsilon = n^2.$$  \hspace{1cm} \text{Equation 2-5}$$

The inductance of the wire conductors in the straight wire structures is inversely proportional to the wire diameter, and is further inversely proportional to the plasma frequency. When the size of the unit cell is held constant while the turn-on frequency is increased, the wavelength decreases and the electromagnetic response moves outside the effective medium regime. As the ratio of the wavelength to the cell size approaches unity, the medium can no longer be approximated as a homogeneous material. At $\lambda/d = 2$, a standing wave exists instead of a propagating wave which is related to the phase advance, $\varphi = 180^\circ$. The length of wire per unit volume must be increased in order for thicker wires to exhibit the same response. Introducing a loop
along the length of the wire, referred to as a loop-wire design, or by introducing a series of loops, such as a coil design, achieves this purpose.

Electromagnetic testing was performed to extract the effective material properties through measurements in an anechoic chamber developed by A. Starr and his colleagues in the Physics Department of UCSD (Figure 2-1). The measurement setup was comprised of an anechoic chamber and an Agilent vector network analyzer (model number 8722ES). The standard S-parameters of the chamber with and without the panel were measured and an adaptive macro was then used to extract the material properties. Other tests have been performed on a focused beam electromagnetic system (Figure 2-2) at CEAM (Center of Excellence for Advanced Materials). The turn-on frequencies were numerically calculated using HFSS (by A. Amirkhizi) and inserted in the theoretical relations to estimate the negative values of the dielectric constant at the stop frequency and lower than the turn-on frequency, since these values cannot be calculated through frequency domain simulations.
Figure 2-1. Anechoic chamber at UCSD Physics Department for EM characterization. [Top] Schematic (courtesy of A. Starr) of sample orientation between microwave transmission and receiving horns. [Lower left] Photo of transmission side of chamber with RAM (radar absorbing material) surrounding all surfaces. [Lower Right] Network analyzer.
2.4 Integration into Composites

To integrate such electromagnetic designs into materials, one needs a periodic material that can accommodate the three-dimensional arrangement of the electromagnetic elements. Fiber-reinforced polymer composites facilitate such
arrangements due to the natural periodicity of their laminate construction. The arrangement of fibers within each layer provides flexibility in orientation, spacing, and geometry of the electromagnetic elements. Each layer may contain elements with orientation in only one direction, as in a unidirectional laminate, or the elements may be woven such that each layer has bi-directional elements. Variation of the spacing of these elements in the thickness (z) dimension of the material is controlled by the sequence in which laminae are stacked to form the laminate.

As an example, arrays of thin, straight wire were introduced into various types of composite materials. Composite panels were made by hand-layup of pre-impregnated woven fabric (prepreg). The samples varied in the type of host material, wire diameter, and number of electromagnetic layers. Host materials included E-glass fibers impregnated with epoxy resin (Bryte 7781 e-glass BT250E prepreg), Spectra® (Baraday prepreg with Honeywell UHMW polyethylene) fibers impregnated with vinyl ester resin, and quartz fibers impregnated with cyanate ester resin (Bryte Astroquartz III 1515 Cyanate Ester Prepreg), chosen for their mechanical attributes and favorable dielectric characteristics. The dielectric constant of Epoxy/E-glass was 4.44 in the microwave frequency regime with a loss tangent of 0.01, and that of vinyl ester/Spectra was 2.45 with a loss tangent of 0.002. Cyanate ester/quartz provided the most balanced overall electromagnetic characteristics with a dielectric constant of 3.01 and a loss tangent of 0.001, where a low dielectric constant and loss tangent are preferable for optimal microwave transmission. The fiber volume fraction for each material was in the range of 50 to 60%. The frequency at which the panels behave as
a plasma depends upon the dimensions of the embedded wire array. Numerical simulations were performed to predict the necessary array for plasma response in the microwave regime. In making each panel, copper wire of 75µm or 50µm diameter was strung across a frame to form the desired pattern and was subsequently encased in layers of prepreg. Panels were processed at elevated temperature and pressure to cure the resin and form the solid composite as shown in Figure 2-3.

A list of representative panels is given in Table 2-1, where each layer denotes one set of wires strung at $90^\circ$ to another set of wires, separated by a layer of prepreg. Samples containing more than one layer of wires had 0.125" of composite material separating such layers.

Table 2-1. Description of representative fiber reinforced composite panels made at CEAM. Composite Materials – Epoxy glass (EG), cyanate ester quartz (CEQ), and vinyl ester Spectra (VES).

<table>
<thead>
<tr>
<th>Composite Material Type</th>
<th>Dimensions (inches)</th>
<th>Wire Diameter (inches)</th>
<th>Wire Spacing (inches)</th>
<th>Number Wire Layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG</td>
<td>6x6x0.125</td>
<td>0.003</td>
<td>0.125</td>
<td>1</td>
</tr>
<tr>
<td>EG</td>
<td>6x6x0.250</td>
<td>0.003</td>
<td>0.125</td>
<td>2</td>
</tr>
<tr>
<td>EG</td>
<td>6x6x0.375</td>
<td>0.003</td>
<td>0.125</td>
<td>3</td>
</tr>
<tr>
<td>EG</td>
<td>6x6x0.125</td>
<td>0.002</td>
<td>0.125</td>
<td>1</td>
</tr>
<tr>
<td>EG</td>
<td>6x6x0.250</td>
<td>0.002</td>
<td>0.125</td>
<td>2</td>
</tr>
<tr>
<td>EG</td>
<td>6x6x0.375</td>
<td>0.002</td>
<td>0.125</td>
<td>3</td>
</tr>
<tr>
<td>CEQ</td>
<td>6x6x0.250</td>
<td>0.002</td>
<td>0.125</td>
<td>2</td>
</tr>
<tr>
<td>CEQ</td>
<td>6x6x0.375</td>
<td>0.002</td>
<td>0.125</td>
<td>3</td>
</tr>
<tr>
<td>VES</td>
<td>6x6x0.250</td>
<td>0.002</td>
<td>0.125</td>
<td>2</td>
</tr>
<tr>
<td>VES</td>
<td>6x6x0.375</td>
<td>0.002</td>
<td>0.125</td>
<td>3</td>
</tr>
</tbody>
</table>
Representative dispersion relations of the dielectric constant in the microwave regime for each of these panels are given in Figure 2-4 and Figure 2-5, comparing both numerical predictions with the experimental results. These graphs show the characteristic trend of changing the dielectric constant from negative to positive values as a result of the plasmon media in a composite panel of each type. Results for the different host materials show similar behavior, though the turn-on frequency is shifted depending on the dielectric constant of the host material and the wire diameter and spacing. Moreover, the results showed that a host material with a lower the original dielectric constant provides a larger frequency bandwidth over which the dielectric constant becomes matched with air (Plaisted et al. 2003c).
Figure 2-3. [Top] Schematic of two dimensional thin wire array. 100µm wires are periodically embedded between composite laminate with layup jig to yield a processed glass/epoxy laminate with array visible inside. [Bottom] Laminating hot presses for processing composite panels.
Figure 2-4. Numerical and experimental characterization of the samples listed in Table 2-1. Data for panels made of the same host composite material and wire diameter are displayed in one chart since their numerical simulations are identical. “Turn-on” indicates the transition between the stop-band and pass-band, or the frequency above which the material transmits electromagnetic radiation. (A) 50µm (0.002”) diameter wires embedded in Cyanate Ester/Quartz composite. (B) 50µm diameter wires embedded in Vinyl Ester/Spectra composite.
Figure 2-5. (C) 75µm (0.003”) diameter wires embedded in Epoxy/E-glass composite (two single layer samples were manufactured and measured for this case). (D) 50µm diameter wires embedded in Epoxy/E-glass composite.
2.5 Coiled Wire Plasmon Media Composites

As an alternative to processing such thin wire into composites, thicker, more robust wire may be incorporated in the form of coiled arrays (Plaisted et al. 2003a). By increasing the length of wire per volume of material, the same degree of inductance may be achieved with thicker wire as with thin straight wire. Textile braiding of reinforcing fibers with wire is an ideal method to integrate the coil geometry into the composite. The braiding process interlaces two or more yarns to form a unified structure. A two-dimensional tubular braiding machine is shown in Figure 2-6, which operates in a maypole action, whereby half of the yarn carriers rotate in a clockwise direction, weaving in and out of the remaining counter-rotating carriers. This action results in a two-under two-over braid pattern. Each yarn makes a helical path around the axis of the braid to create a uniform coil. To integrate the wire coil into such a structure we simply replace one of the fiber carriers with a wire carrier. A comprehensive description of the textile braiding process is given by Ko et al. (1989; 2001).

Braiding wire with the reinforcing fibers results in an electromagnetic element with uniform geometry that maintains its shape under considerable handling and other processing conditions. The braid itself is a tough structure that protects elements woven into the outer sheath, as well as other elements in the core. Thus functional elements (wires and/or perhaps sensors, Figure 2-7) are truly integrated into the fibers of the host composite, rather than acting as inclusions in the matrix phase (Starr et al. 2003; Starr et al. 2004).
In terms of electromagnetic design, braiding allows control of the pitch and diameter of the wire coil such that the electromagnetic properties may be tuned for desired performance. The sense of the coil, as left-handed or right-handed, may also be varied in this process to address issues of chirality (Amirkhizi et al. 2003). The chiral effects of one coil are effectively negated by those of its neighbor coils. The braiding process allows production of coils of both sense by switching the direction of rotation of the wire carrier in the maypole rotation. Two alternative methods to eliminate chirality require that double coils be created. For instance, a coil of one sense may be positioned concentric with a coil with opposite sense. Braiding may accommodate this arrangement as well by over-braiding a left-handed braid on top of a right-handed braid. Otherwise, by including another wire carrier rotating in the opposite direction, a double coil braid consisting of two coils in the same plane may be created if insulated wire is used, such that when the wires cross they do not cause an electrical short at each intersection.
Figure 2-6 [Top Left] Schematic of tubular braiding machine. Fibers and wire (indicated in orange) are spooled from carriers that rotate on a circular track. Fibers may be braided around a center mandrel or other fibers in the core of the braid. [Top Right] Arrow indicates path taken by one yarn carrier in maypole braiding pattern. [Bottom] Photograph of tubular braiding machine at CEAM.
Figure 2-7. Concept drawing of fibrous braid encasing functional elements (red) such as a sensor (courtesy A. Starr).

As an example, braided coil elements have been fabricated with para-aramid (DuPont Kevlar®) reinforcing fiber and polyamide (DuPont nylon 6,6) thermoplastic fiber. The outer braid consists of a single 30 gauge (0.254 mm diameter) copper wire, four ends of 200 denier Kevlar fiber, and three ends of 210 denier nylon fiber. The core of the braid consists of one end of 1000 denier Kevlar fiber and three ends of 420 denier nylon fiber. An illustration is provided in Figure 2-8 showing the constituents of the braid architecture. Nylon is included in the braiding process since it will serve as the polymer matrix of the final composite. Complete penetration of the polymer matrix throughout the fiber preform (fiber wet-out) can be a difficult processing challenge in braided composite materials, due to the inherent tight packing of fibers in the braiding process. This issue has been addressed by developing a commingled braid composite, which integrates the eventual matrix phase as a thermoplastic fiber that is braided along with the structural fibers. Overall, the composite is designed to
have a Kevlar fiber volume fraction of about 50%. Selection of the diameter of the core allows control of the diameter of the coil that is braided around it. The core may be composed of various other elements, including other electromagnetic elements, or perhaps sensors, though in this initial design we incorporate only reinforcing fibers. The pitch of the braids is determined by the take-up and rotation speed of the carriers. The pitch of these coils was maintained at 60° from the axis of the braid.

The implementation of braiding wires and fibers to create coil elements with tunable electromagnetic properties has been verified experimentally. The braided elements had the following specifications: pitch of 60° to the axis, braid diameter of 0.155 cm (0.061in), and wire diameter of 0.0254 cm (0.01in). The braided elements were spaced at a distance of 1 cm (0.39in) in two directions. The plasma frequency of this sample was predicted at $f_p = 6\text{GHz}$ using frequency domain finite element simulations. The braided elements were positioned in a low dielectric test frame and measured within an anechoic chamber. The geometry of the test arrangement is pictured below in Figure 2-9.

One may see in Figure 2-9 that the experimental results showed good agreement with the simulations. The dielectric constant of the structure is measured as a function of frequency from 3-12 GHz, whereupon at 6 GHz the dielectric constant passes through zero. This dispersion relation follows the characteristic trend of the thin straight wire arrays described previously. Between the plasma frequency and the
The braided elements take the form of a laminate by weaving with other reinforcing fibers to form a cohesive fabric. The braids may be oriented in a single direction in each layer or may be woven together bi-directionally. Due to the inherent stiffness of the dry braid, tight weaving patterns in a bi-directional weave, such as plain weave and satin weave, may be restricted since the braid cannot be woven over small intervals without kinking, which compromises the braid structure. This factor is dependent on the braid and wire diameter, where smaller diameters are not subject to such limitations. This limitation is avoided when braids are woven unidirectionally since the fill yarns (weft direction) are able to accommodate such undulation while allowing the braid elements (warp direction) to remain straight. To achieve the desired spacing of the coil array, while maintaining a uniform composite fabric, blank braids may be woven into the layer or inserted between layers. The blank braid is identical to the electromagnetic braid element, however the copper wire is replaced with tow of reinforcing fiber. Additionally, as mentioned above, chiral effects of the coil geometry can be eliminated by alternate placement of a left-handed coil next to a right-handed coil. Such an arrangement can be easily achieved in the braiding and weaving processes. Woven layers are stacked in accord with the electromagnetic design and processed with additional thermoplastic matrix at elevated temperature and pressure to form the consolidated composite.
Figure 2-8. [Top] Schematic of braid cross-section consisting of tows of Kevlar fibers, nylon fibers, and copper wire. [Center] Schematic of outside of braided architecture with 2 up 2 down braid pattern [Bottom] Photograph of braids bidirectionally woven into fabric with additional Kevlar fibers. Coils with opposite sense are woven adjacent to one another.
The braided coil elements have been integrated into a composite and characterized electromagnetically. Braids were fabricated with Kevlar/nylon/wire such that the diameter was 1mm and the pitch of the coil with respect to the braid axis was 60°. The braids were aligned in one direction, and those braids containing the wire coil were spaced 4.2 mm apart within the plane of the laminate. Out of the plane (through the thickness of the laminate) the braids were spaced 1 mm apart. The sense of the coils were arranged in an alternating left-hand and right-hand chiral orientation within the plane of the laminate. Figure 2-10 shows such a panel consisting of Kevlar braids woven into laminates and pressed into a nylon matrix composite, with approximate dimensions of 152 x 152 x 2 mm.

The woven braided composite from Figure 2-10 was measured by focused beam electromagnetic characterization. The panel was first oriented such that the braided elements were aligned with the direction of the electric field of the incident radiation. In this orientation the panel exhibited the predicted plasmon response with a plasma frequency of 18.6 GHz, in very close agreement with the simulation results. The panel was rotated 90° such that the electric field was parallel to the braid axis and exhibited a dielectric constant of about 4, which is approximately the dielectric constant of the host Kevlar and nylon composite.
Figure 2-9. [Top] Test frame containing Kevlar braided with copper wire. Braids are arranged such that adjacent braid elements contain wire coils with opposite sense (inset). [Bottom] Simulated (dashed line) and experimental (circles) characterization of the braided elements.
Figure 2-10. [Top left] Coiled wire architecture integrated with structural Kevlar fibers by braiding. Braids are woven [top right] into fabric [lower left] and laminated into composite plates [bottom right] by hot press.
Figure 2-11. EM characterization of the braided/woven composite showing typical plasmon media response when aligned parallel to the direction of EM radiation. Normal (non-plasma) dielectric response is observed when aligned perpendicular.
2.6 Heating Functionality

The feasibility of using the integrated thin wire arrays to resistively heat the composite has been demonstrated (Plaisted et al. 2003b; Santos et al. 2004). In connection with the integration of healing functionality in to fiber reinforced polymer composites, the heating functionality may be leveraged to induce repair in a thermally activated healing system. Embedded wires are currently used for resistive heating as a method of welding thermoplastic polymers and polymer composites (Eveno and Gillespie Jr. 1988; Jakobsen et al. 1989; Ageorges et al. 2000). Similarly, embedded heating elements have been used to cure the resin matrix in thermoset polymer composites (Sancaktar et al. 1993; Ramakrishnan et al. 2000). Using the same wire diameter and array dimensions as designed for EM functionality, direct current was applied to resistively heat a composite sample.

The testing was designed to achieve a uniform temperature in the range of 80-90°C throughout the sample, since healing in the thermally reversible healing polymer has been demonstrated in this temperature range. Copper wire with a diameter of 100µm was aligned in one direction, spaced 3.175 mm apart, and embedded in a representative glass-fiber/epoxy matrix composite with a fiber volume fraction of about 60%. Three thermocouple wires were included at various depths between the prepreg layers to monitor internal temperatures. The dimensions of the fabricated panel were 15cm x 15cm x 0.32cm. After curing, the copper wire strands that protruded from the edges (48 total) of the panel were retained since they provided
electrical connection. The wires were connected in a series as groups of 4 wires in parallel, as shown in Figure 2-12. Various heating conditions were tested and it was demonstrated that the target temperature could be achieved in about 20 minutes with a power density of 0.073 W/cm², as shown in Figure 2-13. With the insulation removed the power density was increased to 0.2 W/cm² to achieve the same temperature over about 12 minutes.

Figure 2-12. Wiring arrangement for resistively heated composite panel consisted of twelve wire sets connected in series, where each wire set contained 4 copper wires connected in parallel (Santos et al. 2004).

Figure 2-13. Heating curve for 100µm diameter copper wire array embedded in a glass fiber/epoxy composite. Temperature measured with three thermocouples (red, blue, green curves) embedded at various depths. The panel was insulated and heated at a power density of 0.073 W/cm² (Santos et al. 2004).
Figure 2-14. Heating curve for 100µm diameter copper wire array embedded in a glass fiber/epoxy composite. Temperature measured with three thermocouples embedded at various depths (red, blue, green curves). The panel was not insulated and heated at a power density of 0.200 W/cm² (Santos et al. 2004).

Thermal management within the composite is a may be leveraged for a number of applications. In our multifunctional composite, we may utilize this heating function to induce a thermally activated healing process as detailed in the next chapter.

2.7 Acknowledgement

Portions of the contents of this chapter have appeared in “Chapter 12: Multifunctional Materials”, Biomimetics: Biologically Inspired Technologies, Nemat-Nasser, S.; Nemat-Nasser, S. C.; Plaisted, T.; Starr, A.; and Amirkhizi, A. V., published by CRC Press. The dissertation author was the primary author and
investigator of this work. Alireza Vakil Amirkhizi and Syrus Nemat-Nasser are acknowledged for performing the electromagnetic simulations used for modeling of the plasmon structures in this chapter. Anthony Starr and Jack Mock are also thanked for their assistance in measuring and extracting the EM properties of these materials. Diego Arbelaez and Carlo Santos are acknowledged for their contributions to the fabrication of samples and measuring the resistive heating characteristics of the thin wire composites.
3  Crack Healing in Polymers

The crack healing of polymer interfaces has received considerable attention over the past two decades. A material that can heal itself is of great utility where access for manual repair is limited or impossible, as in a biological implant or a material that is launched into orbit in the solar system. Structures made of such a material may have significantly prolonged service life in addition to improved safety if failure mechanisms such as cracking can be repaired in-situ.

Crack healing deals with a fractured material, where the materials on either side of the damaged interface are from the same virgin material. Crack repairs, on the other hand, may also constitute the use of another material, such as an adhesive to “glue” the crack faces back together and hence are not considered healing since the repaired material is significantly different than the original. The definition of healing, as it pertains to this topic, refers to the recovery of mechanical strength across a polymer-polymer interface until it reaches that of the bulk polymer. This chapter provides a review of previous work on the crack healing in thermoplastic and thermoset polymers and composites, including research on self-healing polymer composite systems.

3.1  Polymer Background

To understand the concepts crack healing of polymers, one must first have an understanding of polymers themselves and the characteristics that make such events possible. Polymers are otherwise known as macromolecules since they consist of long
chain molecules with molecular weights ranging from $10^4$-$10^6$. These long chains are made up of a string of monomers, which are the molecular repeat unit identifying that particular polymer. Linear, branched, and the other non-networked polymers generally form amorphous or semi-crystalline polymers with thermoplastic character. Interaction between chains occurs through non-covalent bonding such as hydrogen bonding and chain entanglements. As a thermoplastic, the polymer may be heated to its melting temperature and solidified repeatedly with little change in the properties. In contrast, thermosets consist of cross-linked networks formed by covalent bonding and will degrade, rather than melt, upon heating.

Healing damage within a polymer is most often associated with the softening and flow of material across a damaged interface that occurs upon heating a thermoplastic polymer. This technique is commonly known as thermoplastic welding. Healing in thermoplastic polymers occurs largely due to the restoration of entanglements in the polymer interface. Secondary bonding between chains, in the form of van der Waals or London dispersion forces, is also critical to the healing process. Other bonding, such as hydrogen bonding and chemisorption, can play an important role. Chains are able to diffuse across the interface when heated above the glass transition temperature, $T_g$. The rate of crack healing is strongly time dependent, as the once separated molecular structures diffuse across the interface to form an equivalent bonding state to that of the virgin material. Crack healing in thermoplastic polymer surfaces infrequently results from the re-formation of broken bonds (primary bonds) in the polymer backbone. Typically the polymer chains at the crack interface
have been irreversibly damaged through bond breakage, which results in an average molecular weight significantly lower than that of the bulk polymer. Furthermore, the catalyst for polymerization (through addition or condensation reactions) is not present to re-polymerize the material.

Healing damage within thermoset polymers is typically not possible due to the cross-linked nature of these materials. The cross-link network prevents the polymer chains from diffusing through the material when heated above the \( T_g \). Rather the material begins to thermally degrade when heated excessively and, in contrast to thermoplastics, cannot be returned to its original state. Until recently, there has been no evidence of repairing damage in highly cross-linked materials. An interesting repair scheme has been proposed by White et al. (2001) to embed a healing system within an epoxy polymer. Another system, proposed by Chen et al. (2002), uses a novel reversible bonding approach to repair cross-links.

### 3.2 Crack Healing in Thermoplastic Polymers

Some of the first crack healing studies on thermoplastics were carried out by Jud, Kausch, and Williams (1981) on glassy polymers and similar testing was performed by Wool and O’Connor (1981b). Testing involved the use of compact tension specimens to fracture PMMA (poly methylmethacrylate) with molecular weight ranging from 120,000 – 240,000. The compact tension test was used to induce fracture and the crack was arrested about 10 mm into the sample. Specimens were healed at several temperatures above the \( T_g \), and a brass clip was used to apply
pressure to the fracture surfaces as the material expanded. The results of the PMMA testing are shown in Figure 3-1, for molecular weight samples of 240,000 and 157,000, healed at a temperature about 20° above $T_g$. The primary result of this study showed that the critical intensity factor, $K_{lc}(t)$, followed a trend described by

$$K_{lc}(t) = K_{lc\infty}(t/\tau_0)^{1/4}$$

Equation 3-1

where $K_{lc\infty}$ is the virgin stress intensity factor of the material, and $\tau_0$ the time to achieve that strength. The exponent $1/4$ indicated the healing process was controlled by diffusion. Vacuum drying and polishing the fracture surfaces decreased the speed of healing in PMMA. Wool et al. observed that the crack disappeared visually after about 10 minutes of heating, but recovery of original strength did not occur until about 4,000 minutes. Dimensional change due to heating above the $T_g$ while applying pressure was not reported.
Figure 3-1. Crack healing experiments by on PMMA. Stress intensity vs. time from Wool and O'Connor (1981a).

Many crack healing and polymer welding studies have since ensued. Heating temperature (above the polymer $T_g$) and heating time are the primary factors that dictate this diffusion-controlled process. Other factors such as the molecular weight and surface conditioning play secondary roles.

### 3.3 Crack Healing in Thermoplastic Composites

Crack healing studies in polymer composites have also been studied. Initial work was conducted by Lee and Springer (1987) and Cantwell et al. (1989; 1990) on the welding of PEEK (polyetheretherketone) composites. In particular, Cantwell and co-workers demonstrated the successful lap-shear welding of carbon fiber/PEEK composites. Joint strengths well above 40 MPa were measured for the composite,
which far outperformed the 5-10 MPa joints formed with traditional epoxy adhesive. Furthermore, these welds performed well at higher temperatures, as shown in Figure 3-2. Building upon this work, Davies et al. investigated the healing of cracks in carbon fiber-PEEK composites (Davies et al. 1989). PEEK was investigated because of its outstanding thermal resistance and mechanical strength that makes it an ideal thermoplastic for use in aerospace and other high performance applications.

Delamination between fiber plies was the mode of failure of interest in this study, so double-cantilever beam samples were prepared such that when tested they failed between the fiber plies. Pressure of 1.4 MPa was applied for 5 minutes at various heating temperatures to investigate healing. Figure 3-3 shows the recovery of delamination resistance, measured as fracture energy, at different temperatures. Only half the delamination resistance was measured for healing at 340°C, though for healing at 370°C and above full recovery was observed. For temperatures towards the low end of this investigation, healing times were also investigated. Figure 3-4 shows the recovery of fracture energy versus time for temperatures of 345°C and 360°C. $G_{1c}$ increased as $t^{1/2}$, and using the relation

$$G_{1c} = K_{1c}^2 / E$$

Equation 3-2

where $E$ is the material’s elastic modulus, the fracture energy, $K_{1c}$ is shown to increase as $t^{1/4}$, in agreement with the healing behavior of amorphous polymers based on the diffusion model. However, healing temperatures were above the melting temperature, and over 200K above the $T_g$ for PEEK. PEEK is a semi-crystalline polymer, and thus healing at temperatures slightly above $T_g$ may not be possible, as in amorphous
polymers, due to a lack of randomly oriented chains able to diffuse across the interface. Evidence of this was illustrated in scanning electron micrographs of the fracture surfaces, in Figure 3-5 where pictures (a) and (b) indicate that little contact and diffusion occurred at temperatures around 345° and 360°C for 1 minute of healing. The semi-crystalline nature of PEEK, as well as broken carbon fibers, impairs the establishment of intimate contact and subsequent diffusion. For longer time and slightly higher temperature, where viscosity of the PEEK decreases and may flow around these obstacles, picture (c) illustrates much better contact and interdiffusion occurred and resulted in fracture surfaces that matched those of virgin samples.
Figure 3-2. Lap shear strength of welded PEEK compared to epoxy adhesive joints (Cantwell et al. 1989).

Figure 3-3. Healing of PEEK/carbon fiber composite at high temperature (Davies et al. 1989).

Figure 3-4. Healing of PEEK/carbon fiber composite over short times (Davies et al. 1989).
Figure 3-5. SEM micrographs of PEEK composite interfaces after healing. (a) and (b) Short time/ lower temperature resulted in poor contact and interdiffusion. (c) Longer time/ higher temperature produced optimal weld (Davies et al. 1989).
Evidently there exists a method of healing cracks within thermoplastic polymer composites through a thermally induced diffusion controlled process. However little research has been conducted in this field and, apart from the elimination of defects during initial processing, such healing systems are not presently used to extend the life once the composite is in service. A number of factors may contribute to this situation. In current high performance composite applications, thermoplastics are not widely used due to their inferior mechanical properties compared to thermoset polymers such as epoxies and vinyl esters. The lower stiffness and strength of most thermoplastics do not meet the requirements for use as composite matrices in many applications. Furthermore the processing techniques to obtain a defect-free composite are not as well established due to the high melt viscosity of most thermoplastics that complicates impregnation of the polymer into a fiber preform. The thermoplastics that do possess high mechanical properties, such as PEEK and certain polyimides, also possess a semi-crystalline structure. As mentioned in the previous section, this crystallinity impedes the diffusion of broken polymer chains across a damaged interface at temperatures around the glass transition temperature. Rather, the polymer must be heated close to or above its melting temperature to achieve healing. In many applications, heating a material to such high temperatures, and moreover to a degree that causes the material to melt, is simply impractical. Until the challenges associated with using thermoplastics can be addressed, there exists a need for healing schemes in thermoset polymer materials.
3.4 Crack Healing in Cross-linked Polymers and Polymer Composites

To date there have been few healing studies on healable cross-linked polymers. A similar healing mechanism to thermoplastic polymers is not possible in highly cross-linked materials since the mobility of the broken polymer chains is restricted from diffusing long distances across the cracked interface to re-establish an entanglement network. Experiments that have attempted such healing in a cross-linked epoxy resulted in a recovery of only 1.7% of the virgin fracture strength (Raghavan and Wool 1999).

3.4.1 Autonomic Healing Polymer

In contrast, a clever modification of a cross-linked epoxy with healing properties has been demonstrated by White et al. (2001). Concepts developed by Dry et al. (1993; 1994) were modified and developed by White and led to experimentally quantified proof of a truly self-healing material. White et al. used micron-sized capsules, containing a healing agent, embedded in an epoxy to create a particulate composite. A schematic of the healing process is given in Figure 3-6. The microcapsules were designed to have a modulus lower than that of the surrounding epoxy, such that a propagating crack would be attracted to the inclusion rather than deflecting around it. Analytical and experimental studies showed that this indeed was the case, as illustrated in Figure 3-7, where a crack can be seen to deflect towards a microcapsule. An SEM micrograph, in Figure 3-8, shows a fracture plane that has intersected with a microsphere, which in turn releases the healing agent. The healing agent was a dicyclopentadiene (DCPD) monomer, encased in a urea-formaldehyde
shell. Scattered throughout the epoxy are pockets of catalyst that initiate polymerization of the DCPD to create a highly cross-linked network. The catalyst is a transition metal, known as a Grubbs’ Catalyst, capable of undergoing ROMP (ring opening metathesis polymerization) with the monomer to create this polymer network. The reactants and resulting polymer unit are given in Figure 3-9.

This system is known as a living ROMP, in that some chain ends in the catalyst are unterminated, and may participate in multiple ROMP, thus healing, reactions. Furthermore, the catalyst is capable of triggering polymerization at room temperature in a few minutes with little shrinkage, and does not readily react with other potentially deleterious functional groups. The healing efficiency of this system was tested by tapered double-cantilever beam (TDCB). An initial tension crack was created in the material, at which point the load was removed, and the healing mechanism took effect over a 48 hour period. The samples were then reloaded and the resulting fracture toughness was compared to that of the virgin material system. A representative loading curve is given in Figure 3-10. Initial testing showed a healing efficiency of up to 75% an average around 60%. Optimization of the size and concentration of catalyst and microcapsules on the fracture toughness and healing efficiency of the autonomic composite was later performed. The optimum size and concentration yielded a healing efficiency of up to 90% (Brown et al. 2002a).

The fracture toughness of the healed material increases with incorporation of microspheres, since the presence of microcapsule inclusions provided an additional
toughening mechanism (Brown et al. 2002b; Brown et al. 2004). An increase in the fracture toughness of up to 127% was observed (Brown et al. 2004).

The effect of microcapsules on the fatigue life of the epoxy has also been studied (Brown et al. 2003; Brown et al. 2005b; Brown et al. 2005a; Brown et al. 2006; Jones et al. 2007). The fatigue life was extended by the microcapsules through numerous mechanisms related to shielding the crack tip. Primarily the formation of a polymerized wedge of DCPD at the tip of the crack reduced the stress intensity. There were additional contributions from the viscous flow of the healing agent into the crack plane as well as from adhesive interaction as the DCPD bonded with the crack surfaces. The kinetics of the healing rate in relation to the fatigue rate and applied stress intensity greatly influenced the results. When a rest period was employed to allow polymerization of the healing agent, the fatigue life was extended by 118% - 213%, depending on the applied stress intensity (Brown et al. 2005b). The use of wax encapsulated catalyst may also be used to modify the reaction kinetics to achieve optimal fatigue life extension (Jones et al. 2007).
Figure 3-6. Healing concept of autonomic healing polymer (White et al. 2001).

Figure 3-7. Design of microcapsule to attract the propagating crack (White et al. 2001).
Figure 3-8. SEM micrograph of fractured microsphere (White et al. 2001).

Figure 3-9. Reaction system of the autonomic healing composite (White et al. 2001).

Figure 3-10. Loading curve showing ~70% healing efficiency (White et al. 2001).
Figure 3-11. Effect of microcapsule loading and size on fracture toughness (Brown et al. 2004).

This is indeed a self-healing material, though it is different from most other materials discussed in this review. Rather than healing the host material with a material of the same composition, or activating repair of the fractured material via a liquid, the system developed by White et al. uses a chemically different material to effectively glue the interface together. The healing process in this system is more akin to healing of asymmetric interfaces and the use of adhesives to repair damage. However, since this glue is a component of the virgin material system, it warrants inclusion in this review.

3.4.2 Autonomic Healing Polymer in a Fiber Reinforced Composite

The autonomic polymer has been incorporated into a fiber-reinforced composite to determine if healing attributes demonstrated in the polymer would translate into a polymer composite. Kessler and White used the autonomic polymer as
the matrix in woven E-glass fiber composites (2001). Woven fiber architecture was chosen for its undulating pattern since it provides resin rich pockets in which the microcapsules (diameter 50-200µm) of the self-healing polymer system may reside. Otherwise, in a unidirectional composite, the presence of the microcapsules may disrupt the orientation of the fibers. However, microcapsules were not actually used in this experiment, so self-activation of the healing process was not demonstrated. Rather, composite specimens were fractured by double cantilever beam (DCB) and either manually injected with the premixed monomer/catalyst healing polymer, or manually injected with just the monomer which would react with embedded catalyst. Composites with roughly 30% by volume fiber were compression molded with components (polymer or polymer/catalyst) of the self-healing polymer. The lack of results on the self-activation was due to the complexity of the failure modes in a fiber composite. In addition to simple matrix cracking, fiber/matrix debonding is the dominant mode of failure. Furthermore, penetration of the healing agent into the composite is inhibited by broken fibers.

Overall, the manually injected (premixed) specimens showed reasonable healing efficiency. These composite samples demonstrated only half the efficiency of the autonomic polymer (up to 90%), which was attributed to poor interfacial bond strength between the healing agent and glass fibers. Coupling agents may be expected to improve this problem. Furthermore, microscopy revealed that fiber bridging was an important failure mechanism in the virgin composites, whereas no bridging occurred in the healed samples. The self-catalyzed specimens showed low healing efficiency,
due in part to the above deficiencies, but also another reason. The polymerization step took too long in these samples, such that the monomer was able to diffuse into the damaged matrix before it completed the repair. Thus the rate of polymerization needs to be increased significantly to improve coverage of the healing system on the damaged area.

A further study on the self-healing ability of the autonomic polymer system was carried out by Kessler et al. (2003). The fracture sample was altered to include a taper in the width of the sample that would stabilize crack growth. In addition, these experiments included a self-healing specimen that included both the embedded microcapsules with healing agent and embedded catalyst. Plain-weave carbon fiber was impregnated with different polymer matrices to make three different types of samples (Figure 3-12): 1) neat resin, referred to as reference; 2) neat resin with embedded catalyst, referred to as self-catalyzed; and 3) neat resin with embedded catalyst and healing agent, referred to as self-healing. Fracture testing was carried out on all of the specimens. Fractured samples with only neat resin (1) were manually injected with catalyzed DCPD monomer. Specimens with embedded catalyst (2) were manually injected with DCPD monomer only. Specimens of type (3) were not injected with any outside material. In each case, the specimen were clamped and allowed to polymerize over a 48 hour period. Each specimen was then retested for fracture toughness. Healing efficiencies were measured by comparing to the virgin fracture toughness of the material.
The average self-healing efficiency was around 38%, significantly less than the
self-activated (73%) or reference (99%) samples (Kessler et al. 2003). This was
attributed to a number of factors, including clustering of the catalyst within the resin.
As a result, the DCPD monomer was not catalyzed in rapidly to properly heal the
surface. Rather it was given time to diffuse into the surrounding epoxy matrix prior to
polymerization. In addition, the failure in this scenario consists in part of fracture at
the interface of the fiber and matrix. Thus the microcapsules were not cracked and
therefore DCPD not released. An SEM micrograph, Figure 3-14, contrasts these two
regions, where microcapsules were clearly fractured within the polymer-rich regions
and not in the fiber-rich regions.

The role of temperature was also investigated. Self-healing samples were
healed for a similar 48 hour period at 80°C. These samples exhibited an average
healing efficiency of 66%, with a maximum of 80% (Kessler et al. 2003). This result
illustrated the importance of the polymerization kinetics on the healing efficiency. At
a higher temperature, the rate of polymerization and degree of cure are both increased.
This healing efficiency at elevated temperature is much closer to that observed in the
self-healing polymer alone (maximum 90%).
Figure 3-12. The three testing schemes for the autonomic healing composite. Composite panel is: (a) Injected and catalyzed. (b) Injected and self-catalyzing. (c) Fully self-healing (Kessler et al. 2003).

Figure 3-13. Representative loading curves for the virgin and the autonomically healed composite samples. On average 38% of the original fracture load was recovered (Kessler et al. 2003).

Figure 3-14. SEM micrograph of the fracture surface of a self-healing specimen. The lower right side is an example of fiber/matrix debonding where no microspheres were fractured. Upper left illustrates a region where the crack propagated through the matrix, thus fracturing the microspheres (Kessler et al. 2003).
3.5 Autonomic Healing Fibers in Fibrous Composites

Variations on the concept of incorporating healing agents into fibrous composites have also been developed (Dry and Sottos 1993; Bleay et al. 2001; Trask and Bond 2006; Trask et al. 2007). In these systems, the healing agents are incorporated into hollow fibers, typically made of glass, which fracture under excessive loading, to release the healing agents into the damaged areas of the composite. The arrangement healing agents may take several forms: 1) a one part liquid resin within the hollow fibers; 2) a liquid resin system in the hollow fibers that reacts with catalyst or microencapsulated hardener embedded in the host polymer (similar to the healing system developed by White et al.); or 3) a two part liquid resin system incorporated into different hollow fibers, both of which must break in a suitable stoichiometric ratio, to allow the liquids to mix and react to fill the damaged area (Bleay et al. 2001). A schematic of these three scenarios is presented in Figure 3-15.

A composite utilizing hollow glass fibers filled with a two part liquid resin and hardener system was studied for its ability to restore the flexural strength of a glass fiber composite after damage from indentation (Trask and Bond 2006). The damage decreased the flexural strength of the laminate roughly 25%, and after heating the composite to induce cure of the healing agents, the laminate recovered up to 87% of the flexural strength. Hollow fiber distribution and loading within the composite must be further studied as well as other modes of damage, such as impact-induced damage, to characterize the healing efficiency of this system.
Figure 3-15. Illustration of various hollow fiber self-healing systems (Bleay et al. 2001).

Figure 3-16. Distribution of hollow fibers filled with healing agents within the composite (Trask and Bond 2006).
3.6 Discussion of the Composite Healing Systems

The field of healable composite materials is still in its infancy. The welding and crack-healing of thermoplastics has been thoroughly studied, though primarily in neat polymer systems rather than in fiber-reinforced composites. Only a few studies have attempted to heal large cracks within a thermoplastic (PEEK) resin matrix. Healing at slightly above the $T_g$ in this semi-crystalline polymer was not possible due to a lack of randomly oriented chains able to diffuse across the interface. Rather, the polymer was heated above its melting temperature to allow the polymer to flow and essentially re-mold the interface. Thermoplastic polymers are still not widely used in composite materials due to their limited processing characteristics. Although they tend to be tougher and more ductile, they are typically more prone to fatigue degradation and accumulate microcracks and debonds more rapidly than thermosets (Gamstedt and Talreja 1999).

The autonomic healing system proposed by White et al., and variants of such liquid-releasing embedded systems, are currently the most widely studied methods to heal polymer composites. Certain aspects of their design make them attractive. The healing system may be incorporated into a variety of polymers, typically thermosets, such as epoxy. The repair mechanism is site specific to the area of damage. Most distinguishing is its autonomy; the propagating crack initiates the healing mechanism. The system has its limitations however. Although the catalyst may activate healing multiple times, the liquid monomer is only liquid once and therefore may only heal cracks in a particular region once. A second crack must propagate into a region of
virgin polymer to achieve a second healing event. The healing mechanism is highly
dependent on the amount of microcapsule / hollow fiber loading and the uniform
distribution of the healing components. Currently the size of the microspheres is in
the range of 50-100µm in diameter, and that of the hollow fibers in the range of 35-
100µm. In addition to being subject to cracking during composite manufacture, such
large microspheres are not capable of penetrating into the fiber perform during
composite manufacture. Rather they tend to congregate in the resin-rich interlaminar
regions. Similarly the catalyst tends to agglomerate in the resin. Depending on the
distribution and loading, the crack must grow to a certain length before encountering a
microsphere or hollow fiber. To truly heal microcracks, whose lengths are on the
order of tens of microns, the loading and distribution of healing agents may be
insufficient.

These liquid systems may be further limited in service temperature. For
instance, in the DCPD/Grubbs’ catalyst system, beyond 120°C the catalyst is degraded
and no longer effective. At low temperatures the DCPD monomer will not flow into
the crack plane due to increased viscosity and below -1°C it will freeze altogether.
The effectiveness of the healing is highly dependent on the kinetics of the reaction. If
the temperature is too low the polymerization may never occur, and if too high the
DCPD monomer may vitrify before completely filling the crack plane.

As discussed in the next chapter, a new approach to self-healing has been
introduced that avoids many of the above mentioned problems. The polymer employs
a thermally-reversible Diels-Alder cycloadduct to repair damage in the form of cracks over multiple cycles.
4 Thermally-reversible Cross-linking Polymer

In 2002, Chen et al. (2002) developed a polymer with ability to repair internal cracking. Until that time, there had been no highly cross-linked polymers that could be repaired without the use of additional monomers or surface treatment to repair a cracked interface. Chen et al. accomplished this by synthesizing a polymer based on a thermally-reversible Diels-Alder (DA) and retro-DA cycloaddition. This chapter seeks to review the pioneering work on the thermally-reversible DA polymer by Chen et al., and describes the reaction path for synthesizing the 2MEP4F polymer as performed by the dissertation author.

4.1 Diels-Alder Cycloaddition

Diels-Alder cycloaddition occurs when a conjugated diene combines with an alkene to yield a cyclohexene. The diene contains 4 $\pi$ electrons and the alkene 2 $\pi$ electrons, such that the reaction is often referred to as 4+2 cycloaddition (Vollhardt and Schore 1998). The simplest case is that of cycloaddition of butadiene and ethylene. The butadiene, with its two double carbon-carbon bonds, containing 4 $\pi$ electrons, reacts with the 2 $\pi$ electrons of ethylene to create cyclohexene.

\[
\begin{align*}
\text{1,3-Butadiene} + \text{Ethene} & \quad \xrightarrow{200^\circ C} \quad \text{Cyclohexene} \\
\end{align*}
\]

Figure 4-1. Diels-Alder cycloaddition of butadiene and ethane.
The Diels-Alder cycloaddition is a widely used reaction in organic synthesis. Many polymers involving the DA cycloaddition have been synthesized, though in many cases the retro-DA reaction (reverse reaction) is not observed if the diene and dieneophile are not sufficiently stable on their own. Those polymers with suitable monomer combinations to exhibit the retro-DA reaction have incorporated the DA adduct into the backbone of the polymer (Chujo et al. 1990; Engle and Wagener 1993; Imai et al. 2000). In contrast, the unique aspect of the polymer created by Chen et al. is that all of the monomer linkages, or cross-links, are formed by DA cycloaddition, and furthermore exhibit the retro-DA reaction.

The retro-DA reaction depends on factors such as steric effects of component monomers in addition to secondary orbital interactions. Depending on the type of diene and dienophile and the substituents on those molecules, the equilibrium position of DA-adduct to diene/dienophile shifts as temperature changes. For the maleimide (dienophile) and furan (diene) system, the equilibrium position favors the individual diene/dienophile concentrations as temperature increases (Loy et al. 2000; Chen et al. 2003).

4.2 3M4F Polymer

The polymer consists of a multifuran molecule combined in stoichiometric ratio with a multimaleimide molecule. Initial formulations used a star shaped tetrafur an compound, polymerized with a trimaleimide compound in dichloromethane solvent, which was later removed by vacuum and centrifuge.
UV spectroscopy was used to monitor the degree of polymerization at various temperatures, which is directly proportional to the extent of the DA reaction, shown in Figure 4-3. At 75°C nearly complete polymerization was achieved in three hours. The reversibility of polymerization was also studied by the same technique. Fully polymerized samples were heated to elevated temperatures, such that the retro-DA reaction occurred and the samples were de-polymerized. The de-polymerized structure was fixed in place by freezing in liquid nitrogen and analyzed by UV Spectroscopy. Samples heated to 130°C for 25 minutes the sample de-polymerized by 12%. When heated to 150°C for 15 minutes de-polymerized by 25%. When followed
by heating to 80°C for 1 hour the same sample recovered its original degree of polymerization. This cycle was repeated five times with identical results, shown in Figure 4-4 (Chen et al. 2002).
Figure 4-3. Degree of polymerization vs. time at various temperatures. Open square polymerized at 24°C; closed down arrow at 45°C; open up arrow at 75°C (Chen et al. 2002).

Figure 4-4. Degree of polymerization after various thermal cycling. (A-B) 130°C for 25 minutes then quenched in liquid nitrogen. Roughly 12% of the DA adducts were opened at the elevated temperature. The remaining cycles were for specimen re-polymerized (B-C, D-E, F-G, H-I) at 80°C for 1 hour. The original degree of polymerization was essentially attained each time. Cycles (C-D, E-F, G-H, I-J) were for polymer samples heated to 150°C for 15 minutes then quenched in liquid nitrogen. Roughly 25% of the DA adducts were opened after treatment at this temperature (Chen et al. 2002).

Solid-state C-NMR spectroscopy was used in a similar way to support that the DA and retro-DA reactions occur with thermal cycling. The resonance peaks of positions 3 and 4, shown in Figure 4-5, of the furan monomer were observed at 110
ppm and positions 2 and 5 were observed at 150 ppm. A fully polymerized sample of polymer 3M4F yielded a spectrum in which those resonances were absent. Upon heating the sample to 145°C for 25 minutes and again freezing the structure in liquid nitrogen, the resulting spectra yielded the 110 ppm and 150 ppm resonances of the furan moiety. Re-polymerizing the sample by heating to 120°C erased these resonances, indicating that all of the DA adducts had been restored.

Figure 4-5. Solid state C-NMR. [Top] Resonance values for the furan moiety and furan maleimide adduct. Spectrum (A) is for a fully polymerized 3M4F sample. Note the absence of the 150 and 110 resonance positions visible in the depolymerized spectrum (B). Spectra (C) is that of the repolymerized sample, nearly identical to (A) (Chen et al. 2002).
The weakest bond in the polymer structure is the polymerization/cross-linking bond of the DA adduct. While strong in comparison to other types of non-covalent chemical bonds, this is the first bond to break when the material is loaded to failure or heated above its transition temperature. However, because this bond is reversible, this is also the bond that reforms when the material is cooled below the transition temperature. To test the healing ability of this bond quantitative testing of the fracture toughness was performed. Compact tension samples were notched with a razor blade and loaded in a direction perpendicular to the pre-crack. Complete crack propagation occurred across the sample such that two halves were created. The halves were matched together as close as possible and heated at 120°C to 150°C for two hours under clamping pressure. A slight interface remained in the healed specimen. To test the healing efficiency the samples were then reloaded and the fracture load was measured. Depending on heating conditions, the healing efficiency was measured between 41% and 50%, where a representative loading and re-loading curve is given in Figure 4-6. Furthermore, multiple healing events at or near the same interface were also observed. While respectable healing efficiency was achieved, higher efficiency is expected with improved re-matching of the halves at the fractured interface.
Figure 4-6. (A) Typical loading curve of the virgin polymer versus the healed polymer, showing roughly 57% recovery of strength. Optical micrographs of the fractured (B) and healed (C) samples. (D) SEM micrograph of the scar surface in a healed sample. The scar shows as a white line, though the healed material beneath appears more homogeneous. (E) magnification of (D) (Chen et al. 2002).
4.3 2MEP4F Polymer

Two other bismaleimide monomers have been synthesized and polymerized with the 4F furan monomer and tested for thermal and mechanical properties. They include 1,8- bis(maleimido)-3,6-dioxaoctane (2ME) and 1,8-bis(maleimido)-1-ethylpropane (2MEP) (Chen et al. 2003). The presence of the ethylenedioxy in the 2ME4F polymer causes it to be more compliant than the 2MEP4F and 3M4F polymers. Moreover the stiffness of 2ME4F is greatly reduced when heated above room temperature, with a $T_g$ in the range of 30-40°C. The remainder of this section describes the synthesis and initial healing tests performed on polymer 2MEP4F. This polymer was chosen for further study in Chapters 7 and 8 of this dissertation due to its favorable processing characteristics and mechanical attributes.

4.3.1 2MEP4F Synthesis

An improved method of synthesizing a precursor of the tetrafuran compound has been developed that reduces the processing time. The original procedure required the reaction of acrylonitrile with pentaerythritol to make a tetranitrile compound via Michael addition. The product was converted to a tetracarboxylic compound via hydrolysis (Figure 4-7). The workup procedure required the use of ether to extract this material before crystallization from acetonitrile. Typically this process required weeks of continuous processing to obtain a yield of a few hundred grams. Scale up of this procedure was not easily accessible with standard laboratory synthesis equipment and hood space, and exposure to large quantities of acrylonitrile per reaction was unwanted.
Figure 4-7. Previous reaction scheme for tetracarboxylic compound.

The new process also uses pentaerythritol as the starting molecule, though now it is reacted with succinic anhydride in pyridine (Figure 4-8). The pyridine is later removed by distillation and followed by recrystallization twice from isopropanol. The resulting pentaerythritoltetrakis hydrogen succinate crystals are very similar in composition to the former tetracarboxylic compound with a yield of around 60%. Similar quantities to the previous process may now be obtained in about half the time and there exists potential for further scale-up.

Figure 4-8. Revised reaction scheme for tetracarboxylic compound improves reaction efficiency.
Both tetracarboxylic compounds are further processed into tetrafuran compounds by reaction with thionyl chloride in dichloromethane. After removing the solvent, further distillation is performed with benzene. The residue is dissolved in dry tetrahydrofuran at 40°C. Freshly distilled furfuryl alcohol and pyridene are added dropwise over a period of 1 hour to afford a white precipitate that is later filtered out (Figure 4-9). The liquid portion is then concentrated on a rotary evaporator and the residue chromatographed in alumina using ethyl acetate as solvent.

![Figure 4-9. Reaction of tetracarboxylic compound into tetrafuran.](image)

A bismaleimide compound has also been developed which melts at a lower temperature than the trimaleimide and does not require dichloromethane for polymerization with the tetrafuran. Instead this maleimide monomer may be dissolved in the furan monomer at elevated temperatures. The monomer is 1,8-bis(maleimido)-1-ethylpropane, abbreviated 2MEP, and melts at 82-84°C (Chen et al. 2003). Its synthesis procedure follows that of other bismaleimide compounds, whereby a diamine compound is reacted with maleic anhydride in dimethylformamide at about...
75°C (Figure 4-10) (Kossmehl et al. 1995). Nickel acetate tetrahydrate, acetic anhydride and triethylamine are added to complete the reaction. The reaction may be completed in 24 hours though the workup procedure requires multiple purification steps in silica gel and activated charcoal and crystallizations from ethyl acetate and hexane.

![Chemical structure](image)

Figure 4-10. Synthesis of 2MEP bismaleimide compound.

The 2MEP monomer has been polymerized in stoichiometric proportion with the tetrafuran compound to form polymer abbreviated as 2MEP4F. Similar solid-state C NMR analysis was performed to monitor the Diels-Alder cross-linking and retro Diels-Alder reactions, shown in Figure 4-11.
Figure 4-11. Solid state C-NMR testing of 2MEP 4F polymer, with similar results to Figure 4-5 (Chen et al. 2003).
4.3.2 2MEP4F Preliminary Healing Efficiency

The healing efficiency of the 2MEP4F polymer was also characterized through compact tension testing (Chen et al. 2003). To arrest crack propagation in these tests, a hole was drilled into the middle of the specimen. In this way the cracks were arrested before fracturing the material into two halves and allowed more accurate alignment of the fracture surfaces during the healing treatment. However, the fracture toughness measured in these tests was affected by the presence of the hole and may not represent a true measurement of fracture toughness. These tests did however provide a quantitative comparison between the original fracture load and that after healing. Healing was carried out at 115°C for about 30 minutes within an oven with pressure applied by a clamp. A representative load displacement curve is given in Figure 4-12. Averaging over three tests, the material was able to recover 81% of its original fracture load. Furthermore, when the same healing procedure was applied a second time, the material recovered an average of 78% of the original fracture load, indicating that the material could be repaired multiple times. It was noted that the crack usually propagated along the same crack plane. The healing efficiency of 2MEP4F has been more thoroughly characterized through a different method, as detailed in Chapters 7 and 8.
4.4 Summary of the Diels-Alder Polymer

A cross-linked polymer with thermally-reversible covalent bonds, such as that created by Chen et al., offers many attractive features. The testing by Chen et al. on macro-cracked neat polymer samples showed excellent potential for recovery of strength after healing. Moreover, healing was carried out multiple times on the same sample. These results served as the motivation for the research described in the remaining chapters of this dissertation, which describe new methodologies to measure the crack healing efficiency in neat 2MEP4F polymer as well as 2MEP4F reinforced with continuous carbon and glass fibers.
4.5 Acknowledgement

The dissertation author would like to thank Professor Fred Wudl, Dr. Xiangxu Chen, and Dr. Sunny Skaria of the UCLA Exotic Materials Institute for sharing their expertise on the synthesis of these novel polymers.
5 Mechanical, Thermal, Electromagnetic and Other Measurements of 3M4F and 2MEP4F Polymers

This chapter describes a number of experiments to characterize the mechanical, thermal, electromagnetic, and other properties of the 3M4F and 2MEP4F polymers performed by the dissertation author.

5.1 Preliminary DCDC Testing

Preliminary experiments were performed on polymer 3M4F to demonstrate the fracture and healing using a specimen analogous to the DCDC geometry. These tests represented the first healing demonstration on samples where the crack was arrested prior to complete fracture of the sample. Due to limited 3M4F availability, samples were machined to 0.635 x 0.381 x 0.508 cm dimensions with a 0.203 cm diameter hole penetrating through the middle. Two notches were cut into the hole to initiate the crack on opposing sides of the hole. The samples were cooled in liquid nitrogen and immediately loaded in compression by a screw-driven vise in the direction of the machined notch. The applied load caused cracks to grow from the notches in a controlled manner in the direction of the applied load. Cracked samples were then placed in a spring device that applied compression normal to the crack faces so as bring the crack faces into contact. Samples were heated for 6 hours in the range of 84-87°C under a nitrogen atmosphere with pressure applied normal to the interface, the crack was observed to disappear, indicating healing. In these cases, no visible scar remained, apart from the initial starter notch. These tests were only qualitative in
nature. However, it appeared that the crack had been completely repaired and visually the material had been restored to its original state. Figure 5-1 shows representative photographs before and after the healing event.

Figure 5-1. [Top] – Schematic of miniature DCDC geometry used in preliminary testing. [Middle] - Diagonal view of optical photograph taken at 20X magnification of representative 3M4F sample after cracking. [Bottom] - Sample after healing where crack faces have disappeared leaving only starter notches and pre-drilled hole visible.
5.2 Compression Testing

Compression tests at high and low strain rate were conducted to compare the 3M4F and 2MEP4F polymers to other structural thermoset and thermoplastic polymers. Comparison polymers included vinyl ester (Dow Derakane 411-350 with 1.5% MEKP), epoxy (Devcon DGEBA resin), PEEK (polyetheretherketone) thermoplastic and nylon 6,6. All polymers were machined into cylindrical samples of diameter 0.89 cm and length 0.57 cm. Low strain rate tests were performed on a MTS universal testing machine at a strain rate of $10^{-3}$ per second. High strain rate tests at 2,000 per second were performed using the split Hopkinson bar technique, shown schematically in Figure 5-2 (Nemat-Nasser et al. 1991). All of the tests were performed at room temperature, and the ends of the samples in contact with the testing equipment were lightly lubricated with lithium grease.

![Figure 5-2](image-url)  
Figure 5-2. Schematic of classical compression split Hopkinson bar technique for high strain rate testing.
Figure 5-3. Compression testing of 3M4F and 2MEP4F polymers in comparison to other engineering polymers. [Top] High strain rate testing at 2000 sec⁻¹. [Bottom] Low strain rate testing at 0.001 sec⁻¹.
At a strain rate of 2,000 per second, the 3M4F polymer proved to be the stiffest material. Furthermore, the 3M4F polymer showed the greatest increase in strength at the higher strain rate, where the ultimate strength increased by over two and a half times the value at low strain rate. At high and low strain rate the 3M4F and 2MEP4F polymers performed similarly to epoxy in terms of modulus, yield strain, ultimate strain, and the overall failure behavior, although the 2MEP4F polymer was slightly less stiff and strong compared to the 3MEP4F. All of the thermosets followed a similar mechanical loading follow a similar trend due to their highly cross-linked structure. The 3M4F and 2MEP4F polymers also followed this trend.

5.3 Thermal Analysis

The section summarizes a series of thermal analysis experiments to study the thermal properties and transitions within the 2MEP4F polymer system. Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA) techniques were used to understand the thermal transitions and coefficient of thermal expansion (CTE) of the polymer.

5.3.1 Differential Scanning Calorimetry

DSC ramps were carried out at a constant heating rate and the amount of energy required to raise the temperature of the sample and a reference aluminum pan was measured. The endo- and exothermic processes within the material were then observed. Temperature Modulated DSC (TMDSC) employs a linear temperature ramp with a sinusoidal overlay to distinguish between transitions based on kinetics and heat
capacity (TA Instruments 1998). The heat flow may be deconvoluted into components termed *non-reversing*, which include kinetic effects such as chemical reactions, and *reversing*, which relate to changes in the heat capacity such as the glass transition ($T_g$) and melting/crystallization. In the present experiments, TMDSC was carried out by heating the sample at 3°C/minute with modulation of ±1°C every minute within a nitrogen environment. The DSC used was a TA Instruments Model 2920 and utilized aluminum pans for containing the samples.

### 5.3.1.1 2MEP4F Polymer

A thermal scan of reacted 2MEP4F polymer is shown in Figure 5-4. From the *reversing* component of the heat flow, the $T_g$ is evident in the range of 87 - 101°C. The onset, defined by the intersection of the tangents to the upper horizontal and sloped portions of the curve, occurs around 87°C. The end of the transition, at 101°C, is likewise defined by the intersection of tangent lines to the lower horizontal portion of the curve with the sloped portion. The inflection point of the steep portion of the curve, used here to define the $T_g$, occurs at about 93°C.

The non-reversing component shows some features between 83°C and 95°C related to kinetic processes. Likely these features correspond to the lone furan and maleimide moieties gaining conformational mobility, due to the glass transition, such that they interact and react through DA cycloaddition. These furan and maleimide groups may have been present due to incomplete cure or perhaps from cracks (retro-
DA reaction) within the polymer sample introduced while breaking off a small piece to obtain the DSC sample. In the range of 110°C to 130°C the polymer has undergone a transition that corresponds to retro-cycloaddtion of the DA bonds.

Figure 5-4. Temperature modulated DSC of polymer 2MEP4F.

The reversibility of the DA bond can be further observed in the DSC scan of Figure 5-5. The lower curve (labeled with the open squares) is that of a near fully polymerized 2MEP4F sample. The main transition is that between 110°C and 130°C, which corresponds to the DA bonds disconnecting. The top curve (indicated by the closed circles) is obtained when the disconnected structure is frozen in place (i.e. with liquid nitrogen) and then heated through the same temperature ramp. Although the temperature is below 120°C, the furan and maleimide groups have not reconnected since they were frozen into place. Rather, the disconnected furan and maleimide
groups must gain enough mobility through increased temperature to interact, which is observed at the peak at about 80°C, when they reconnect and give off energy in an exothermic reaction. This top curve is also observed when the polymer has not fully reacted during the initial mixing of the monomers.

Figure 5-5. Results of Differential Scanning Calorimetry on 2MEP4F polymer. Lower curve (labeled with the open squares) of near fully polymerized 2MEP4F that shows main transition at around 120°C when DA bonds undergo retro-DA reaction and the cycloadduct breaks into the furan and maleimide moieties. If this structure is frozen in place, and the resulting partially polymerized 2MEP4F (top curve indicated by closed circles) is heated again, the furan and maleimide moieties reconnect above 80°C in exothermic reaction.
5.3.1.2 2MEP4F Composites

Experiments were performed to understand if the thermal transition of the 2MEP4F polymer was affected by the incorporation of carbon fibers (Toray T300) or glass (AGY S-2) fibers in forming a composite. Figure 5-6 compares temperature modulated DSC scans of polymer 2MEP4F with and without carbon composite fibers. These samples were extracted from fiber-containing or resin-rich portions of the same specimen. The reversing and non-reversing heat flows show very similar behavior. Figure 5-7 shows the same case for S-2 glass fibers. The characteristic peaks and transition temperatures are very similar. There is however some variation between transitions of the neat polymer extracted from the glass composite and carbon composite samples. These samples were made from separate batches of maleimide and furan monomers, which may indicate some variability in the synthesis process. Two characteristic transitions occur at around 83°C and 95°C in the non-reversing curves of the neat polymer from the carbon samples but do not occur in the neat polymer from the glass fiber samples. This may be attributed to the fiber chemistry or sizings on the carbon fibers that may have been introduced into the polymer during infusion.
Figure 5-6. DSC scan of reversing and non-reversing heat flows of 2MEP4F polymer and carbon composite with 2MEP4F polymer.

Figure 5-7. DSC scan of reversing and non-reversing heat flows of 2MEP4F polymer and S-2 glass composite with 2MEP4F polymer.
5.3.1.3 2MEP and 4F Monomers

DSC scans of the individual bismaleimide (2MEP) and furan (4F) monomers were shown in Figure 5-8 and Figure 5-9, respectively. These scans are also shown relative to the 2MEP4F polymer in Figure 5-10. The maleimide monomer has a defined melting point at 89°C, which is above previously reported values of ~84°C, perhaps due to small amounts of impurities in the sample (Chen et al. 2003). Characteristics of the non-reversing and reversing curves of the individual monomers are not observed in the polymer, which indicates most of maleimide and furan have reacted and no longer show characteristics of individual components in the polymer.

Figure 5-8. DSC scan of 2MEP bismaleimide monomer.
Figure 5-9. DSC scan of 4F furan monomer.

Figure 5-10. DSC scans of furan and bismaleimide monomers relative to the 2MEP4F polymer.

Figure 5-11 shows DSC scans of the 2MEP4F polymer in comparison to the carbon fiber used in fabricating the 2MEP4F/carbon composite. The reversing heat flow curves for the polymer and composite are very similar. The non-reversing curves however begin to diverge at about 85°C, such that the composite curve is offset in the
positive direction, over the same region that the carbon fiber curve exhibits a positive shift. The reason for this shift may again be due to thermal transitions associated with sizing on the fibers.

Figure 5-11. DSC scan of 2MEP4F polymer, carbon fiber, and composite fabricated from these two components.

5.3.2 Dynamic Mechanical Thermal Analysis

The DMTA technique is typically used to measure the thermoelastic and viscoelastic properties of polymers by applying an oscillatory force and measuring the resulting displacement. The dynamic storage modulus, $E'$, and dynamic loss modulus, $E''$, may be derived from these measurements. The transition between elastic (glass-like) and viscoelastic (rubbery) regimes is indicated by monitoring the peak in the tangent of the phase difference between the loss and storage modulus, referred to as
the $\tan \delta$, and is often used to define the glass transition of the polymer. Quasi-static experiments may also be performed in the DMTA to measure properties such as thermal expansion and relaxation of the polymer. In the present work, thermal analysis with the DMTA was performed with single cantilever bending of rectangular beams in multi-frequency mode. The DMTA used was a TA Instruments Model 2980. In single cantilever bending, the specimen is clamped between the oscillating bracket (center) and a fixed bracket, as shown in Figure 5-12. The specimens were heated from $35^\circ$ to $135^\circ$C at $3^\circ$C/minute while oscillating at 1 Hz and $30\mu$m displacement.

![Figure 5-12. Diagram of cantilever bending grips for DMTA (TAInstruments 2002).](image)

### 5.3.2.1 2MEP4F Polymer

The scan of the neat 2MEP4F polymer is shown in Figure 5-13. The material exhibited a glass transition, measured at the inflection point of the $E'$ curve, at about $100^\circ$C, and $107^\circ$C by measurement of the peak in the $\tan \delta$. This value is significantly higher than the $T_g$ measured by DSC (inflection around $93^\circ$C), however this is not uncommon in comparing transitions measured by DMA vs. DSC. The peak in the $\tan$
$\delta$ is again higher since it represents the end of the transition from glass-like to rubbery response. That the peak in the $\tan \delta$ occurs about 7°C higher than the inflection point in the $E'$ curve indicates an extended temperature window over which the polymer undergoes the transition. Initially there may be conformational motion of groups around the polymer backbone that begin to move at the onset of the transition around 85-90°C and further loss of modulus occurs due to the retro-DA reaction.

![Figure 5-13. DMTA of neat 2MEP4F polymer.](image)

The neat polymer results are comparable though slightly higher in $T_g$ to DMTA results of polymer 2MEP4F reported by Chen (2003). Chen mixed the 2MEP maleimide monomer in powder form into the 4F furan monomer, which does not achieve the same degree of mixing and conversion to polymer as mixing the monomers in the liquid state, as performed here. With a higher degree of polymerization (cross-linking) the $T_g$ is also increases, which is reflected in the results shown in Figure 5-13.
5.3.2.2 2MEP4F Carbon Composite

The composite of 2MEP4F with carbon fiber, in a [0/90]_sym layup, was analyzed by the same DMTA method. The \( T_g \) in the composite was measured at about 118°C at the inflection point and about 119°C at the peak in the \( \tan \delta \). These values are higher than the neat polymer results by about 10°C and are also much closer together. The onset of the transition in the neat polymer observed around 90°C is not observed until about 114°C in the case of the composite. The high fiber volume fraction (~60%) of the stiff carbon in the composite could mask the initial softening in the polymer, or it may be due to an interaction between the carbon and polymer. The seeming increase in \( T_g \) may be due to sizing agents and/or the formation of an
interphase region between the CF and the polymer that restricts conformational motion. The large drop in modulus at 114°C is likely due to the retro-DA reaction.

![Graph showing DMTA of 2MEP4F/carbon composite.](image)

**Figure 5-15.** DMTA of 2MEP4F/carbon composite.

### 5.3.3 Coefficient of Thermal Expansion

DMTA was used in tension to measure the CTE of neat polymer 2MEP4F. The sample was heated from -120°C to 70°C in increments of about 31.5°C. At each step the sample was held isothermal for 45 minutes while the dimension was measured. The change in sample length versus temperature is shown in Figure 5-16. Averaged over this temperature range, the CTE of the polymer was about 41μm/m°C.
Figure 5-16. CTE measurement of polymer 2MEP4F.
5.4 Interfacial Shear Strength

The interfacial shear strength (IFSS) of 2MEP4F should be characterized with frequently used composite reinforcing fibers, such as carbon and glass, and their sizing agents. The single fiber fragmentation test may be used for such a measurement though it requires a significant amount of polymer to make each specimen (Herrera-Franco and Drazal 1992; Herrera-Franco et al. 1992). An alternative method is that of the microbond test, in which a droplet of polymer, on the order of tens of micron in diameter, is placed on a single fiber and the load required to debond the droplet from the fiber is measured (Miller et al. 1987; Miller et al. 1991). To minimize the amount of 2MEP4F material required for interfacial testing, the microbond test was selected to measure IFSS and a fixture was designed and fabricated for these tests. The fixture, shown in Figure 5-17, was based on two bending beams instrumented with strain gages to allow measurement of the small loads required to shear a single drop of resin from the surface of a single fiber.

Droplets of 2MEP4F with diameters around 50-150 µm were deposited on single carbon and glass fibers. The 2MEP and 4F monomers were heated to about 90°C, mixed for 30 seconds and applied to the fibers with the aid of a microscope. The samples were held at about 100°C to ensure complete polymerization. When tested, the fibers would break prior to debonding of the microdroplet, due in part to the high interfacial shear strength between the polymer and fiber, as well as the relatively large size of the droplet. Debonding prior to fiber breakage was observed on two droplets whose diameters were about 50 µm. The facilities to fabricate multiple
samples with uniform droplet diameters less than 50 µm were not available during this work. A major obstacle in forming the microdroplets was the rapid polymerization of the two monomers (less than three minutes) at this temperature. Since many tests are required to make a statistically valid approximation of the interfacial shear strength, further testing by this method was not pursued. Polymerizing the monomers in solvent at lower temperatures may slow the reaction and to facilitate placement of the tiny droplets on the fibers, and due to their large surface area, the solvent may escape before complete polymerization. If such a method is still unsuccessful, the author recommends characterizing the interfacial shear strength by the single fiber fragmentation method when greater quantities of the 2MEP4F polymer are available.

Figure 5-17. Schematic [left] of microbond apparatus [right] to measure interfacial shear strength of 2MEP4F polymer with composite fibers.

5.5 Viscosity Determination

Viscosity measurements were recorded for component monomers 2MEP and 4F. A Brookfield model CAP 2000 cone and plate type viscometer with was used to measure viscosity. The cone selected for these measurements had a radius of 1.511cm
and cone angle of 0.45°. Initial calibration of the meter was performed with a standard oil as prescribed in the calibration procedure for the meter (Brookfield 2002).

The minimum temperature at which the two monomers may be combined as liquids is determined by the melting temperature of the 2MEP monomer (~84°C). Minimizing the reaction temperature extends the time to gelation of the polymer. Hence the optimum processing temperature exists in this 84-90°C range and thus knowing the component viscosities around this range is of interest. The heating limit of the Brookfield CAP 2000 is in the range of 75 to 80°C. In order to obtain viscosity measurements while the 2MEP is liquid, monomer 2MEP was initially heated to about 10° above its melting point while the viscometer was pre-heated to its maximum heating temperature around 75°C. The initial viscosity readings as the temperature equilibrated provided a general value for the viscosity in this temperature range. The viscosity was averaged from three readings taken within the first 10 seconds of the material contacting the viscometer cap/cone. The average viscosity was 50 centipoise (cP).

Similar measurements were performed for monomer 4F over a wider temperature range, since this monomer has a much lower melting point. The average of three readings was recorded over the temperature range from 50°C to about 80°C. The viscosity ranged from 1130 cP at 50°C and decreased exponentially to 154 cP at
about 80°C. The viscosity between 70-80° appeared to be leveling out such that further increases in temperature would not dramatically lower the viscosity.

Viscosity measurements of the polymerization were unsuccessful due to the rapid gelation of the monomers around the 80°C temperature. Adequate mixing of the monomers and transfer to the viscometer did not allow sufficient time for a measurement to be made without jeopardizing the integrity of the equipment. Rather an estimate of the initial viscosity upon mixing the two monomers can be calculated from a rule of mixtures:

\[ V_{4F} (\eta_{4F}) + V_{2MEP} (\eta_{2MEP}) = \eta_{2MEP4F} \]  

Equation 5-1

where \( V_{4F} \) and \( V_{2MEP} \) are the furan and maleimide stoichiometric volume fractions, respectively, and \( \eta_{4F} \), \( \eta_{2MEP} \), \( \eta_{2MEP4F} \) are the furan, maleimide, and polymer viscosities at ~80°C, respectively. This approximation disregards the increase in viscosity due to reaction of the two monomers. With a 60% furan to 40% maleimide reaction the initial pre-polymer viscosity is about 112 cP.
Figure 5-18. Viscosity measurements for 4F furan and 2MEP bismaleimide monomers.

Figure 5-19. Schematic of cone and plate viscometer.
5.6 Dielectric Measurement of Polymer 3M4F

Polymer 3M4F was characterized for its dielectric properties in the GHz range through a perturbation measurement in a TE 101 cavity. Equipment used for this measurement included an Agilent 8722ES Network Analyzer, Gordon Coupler\(^4\), a TE 101 Cavity, and a W.L. Gore SMA to N cable. These components are pictured in Figure 5-20. A description of the Gordon Coupler and its operation is given by Gordon (1961) and that of the TE 101 cavity by Poole (1993).

![Gordon Coupler and network analyzer for measuring dielectric properties.](image)

A rectangular parallelepiped of dimensions 4 x 6 x 8.75 mm was machined from a casting of 3M4F polymer. The resonant frequency of the empty TE101 cavity was measured at 9.3GHz. The polymer sample was then placed in the corner of the resonant cavity and lightly held in place with silicone grease (dab 1 mm in diameter).

\(^4\) Constructed by Roger Isaacson, UCSD Physics Department
between the cavity wall and the largest face of the sample. The resonant frequency of
the cavity with the sample was then measured.

The dielectric constant of the material under test was inferred from a shift in
the resonant frequency of the empty and loaded (perturbed) cavity. This shift is
illustrated in Figure 5-21. A simulation of the dielectric constant for the TE 101
cavity with approximate dimensions was calculated in Microwave Studio over the
frequency range of interest as indicated in Figure 5-22.\textsuperscript{5} This simulation did not
account for the radius on the inside corners of the actual cavity. The resonant
frequency of the empty cavity was calculated to occur at 9.4 GHz though the measured
resonant frequency was 9.3 GHz. As a result, the simulated relationship between
frequency and dielectric constant as it relates to the actual experiment was offset by
0.1 GHz. The resonant frequency of the TE 101 cavity with the 3M4F polymer
occurred at 9.17 GHz. Shifting the value to 9.27 GHz, the approximate dielectric
constant would be around 2.8 \pm 0.3. The error in this measurement was based upon
measuring the dielectric constant of other well characterized materials, such as
polytetrafluoroethylene and cross-linked polystyrene (Rexolite \textsuperscript{®}).

\textsuperscript{5} Generated by Dr. Syrus Nemat-Nasser in Microwave Studio\textsuperscript{®}
Figure 5-21.  Shift in resonant frequency of TE 101 cavity when loaded with 3M4F sample.

Figure 5-22.  Simulated frequency vs. dielectric constant for mode 1 resonance in TE 101 cavity.
The Quality factor, $Q$, for the cavity is defined as

$$Q = \frac{\omega_0}{\delta \omega}$$

Equation 5-2

where $\omega_0$ is the measured resonant frequency and the full width half minimum at that frequency is $\delta \omega$. The loss tangent of the material is based on the $Q$ factor. The empty cavity had a $Q$ of around 3811, whereas that containing the 3M4F polymer was 945. The loss tangent in the range of 10 GHz for the 3M4F polymer is around 0.0085.

5.7 Polymer 2MDPM 4F

A commercially available maleimide monomer has also been investigated for polymerization with furan monomer 4F. Monomer 4,4’-Bis(maleimidodiphenylmethane), which is abbreviated here as 2MDPM, is commonly used in the production of bismaleimide polymers. Due to its two phenyl rings, this molecule is stiffer and has a melting point around 152°C. To process this maleimide with the furan monomer both monomers must be heated above this temperature and subsequently mixed. Two problems arise with this process. The bismaleimide may homopolymerize at a temperature only 10K higher than the melting temperature (Sava and Fulga 2003). Hence this monomer may solidify on its own if the temperature is not carefully controlled. Furthermore, reacting the monomers at this temperature results in a very rapid reaction such that complete mixing can be difficult before the polymer reaches the gel state. In terms of processing into a composite preform, this poses significant challenges. Attempts to polymerize 2MDPM and 4F monomers were unsuccessful due to the rapid formation of a pre-polymer before adequate mixing.
could occur. Polymerization of 2MDPM monomer with furan in dichloromethane solvent was also attempted, with the intent to later remove the solvent by vacuum. Again the reaction kinetics of these monomers was such that the solvent was not completely removed before the polymer gelled; hence the dichloromethane was trapped in the polymer, rendering it soft and pliable in comparison to the other formulations.

![Structure of 2MDPM monomer](image)

Figure 5-23. Structure of 2MDPM monomer.

### 5.8 Acknowledgement

The dissertation author thanks Jon Isaacs for his assistance in the split Hopkinson bar measurements and Dr. Syrus Nemat-Nasser for his guidance in the use of the Gordon Coupler. Marc Robinson is also thanked for his assistance in the viscosity measurements.
6 Experimental Technique for the Measurement of Fracture and Repair of Healable Polymers

The recent development of self-healing polymers has introduced a need for accurate methods to quantify the fracture and healing of these unique polymers. Testing in the literature has typically utilized standard specimen geometries for measuring the fracture toughness of materials, such as the compact tension (CT) specimen. Tension is applied to create a mode I crack which tends to propagate in an unstable manner, such that the specimen is fractured into multiple pieces. With regard to healable polymers, this geometry leaves something to be desired in that accurate rematching of the fractured interface for subsequent healing and re-measurement poses problems that may lead to inaccurate assessment of the healing efficiency. Crack arresting modifications, such as a hole drilled along the predicted crack plane, may be used to keep the specimen intact after fracture, though the measurement of fracture toughness may be inaccurate due to the influence of the hole. A variation of the CT specimen, called the tapered double cantilever beam (TDCB) specimen, involves the incorporation of a taper into the profile of the sample geometry to resist crack opening displacement as the crack propagates along the fracture path. However, often the crack propagates the full length of the specimen in this geometry as well.

To address these problems, a new sample geometry has been utilized for fracture and healing measurements. The double cleavage drilled compression (DCDC) sample was originally applied to the study of fracture in relatively stiff, brittle materials such as glass. The mathematical models to describe fracture in this
specimen were developed based on experiments with these materials and do not adequately describe the fracture characteristics in brittle polymers. This chapter presents a thorough characterization and accompanying model of the fracture characteristics of brittle polymer PMMA (poly methylmethacrylate) in the DCDC geometry. The results of this model were essential to the development and understanding of a suitable DCDC sample geometry to study the fracture and healing characteristics of polymer 2MEP4F, as discussed in Chapter 7.
6.1 Introduction

The double cleavage drilled compression sample (DCDC) refers to a column of a rectangular cross-section, with a circular hole drilled through its center, that is subjected to axial compression. This technique provides many advantages in studying the fracture toughness of brittle materials. Janssen (1974) originally introduced the specimen for measuring the fracture toughness of glass. Under a uniform axial compression, a tensile stress is produced at the crowns of the hole, as indicated in Figure 6-1. Once the tensile stress reaches the fracture strength of the material, a stable mode I crack is generated at each crown, propagating along the mid-plane of the sample as the axial compression is increased. When the crack reaches a critical length, it may jump and extend the entire length of the sample with a minute increase in the axial compression, being arrested close to the ends of the column due to the geometric constraint imposed by the frictional forces acting over the ends of the sample in contact with the loading platens. By careful displacement-controlled loading, the crack growth can be controlled to a certain extent.

We have identified this specimen geometry to be ideal for studying the healing of polymers since the fractured interface may be closely repositioned to its original location for the healing process, after which it is re-fractured in order to measure the fracture toughness of the healed crack. As a starting point, we have performed a series of quantitative tests on PMMA samples, and have sought to model the tests using expressions reported in the literature, e.g., by Sammis and Ashby (1986), Warren (1987), Michalske et al. (1993), He et al. (1995), and Jenne et al. (2003). The
results of these published models did not correspond well to our experimental data, whereas a simple model that combines a suitably modified version of two estimates, one based on a short-crack and the other on a long-crack approximation, correlates well with all our experimental results and yields a reasonable range of values for the fracture toughness. In seeking to use the published models, we have realized that the two-dimensional linear elasticity solutions, used to obtain results in several of the above mentioned models, do not actually apply to the present problem, since compression-induced axial crack growth in DCDC samples is strongly affected by the lateral deflection of the column. These kinematical quantities are ignored as second-order terms in linear elasticity, rendering linear elasticity an inappropriate tool for modeling the compression-induced axial fracturing in beam-column samples. This and related issues are examined at the end of the chapter. While Sammis and Ashby (1986) do seek to include the beam-column effects, their result does not apply to large crack lengths relative to the hole radius; see the Discussion Section 6.6 for further detail.
Figure 6-1. DCDC specimen with central hole. Solid lines emanating from the crowns of the hole indicate the shape and location of the initial pre-cracks. Upon loading, pre-cracks connect and propagate (dotted lines) towards the direction of applied compression.

In Section 6.2 the experimental procedures and sample dimensions are presented. The experimental results are given in Section 6.3. In Section 6.5 we have detailed our modeling procedure for both the short- and long-crack solutions, and the results are compared with those of our experiments. A comparative discussion is then presented in Section 6.6, and the resulting conclusions are outlined in Section 6.7. The results of the healing polymer are reported in Chapter 7.
6.2 Experimental Procedure

The DCDC specimens in this study were machined from Chemcast Acrylic poly(methylmethacrylate) plates. Sample geometries with half-width to hole radius \((w/R)\) ratios of 2, 3, 4, and 5 were investigated. The dimensions, as labeled in Figure 6-1, were as follows: hole radius, \(R\), ranged from 1.6 to 2.6mm, sample half-width, \(w\), from 4mm to 8mm, thickness, \(t\), 11mm, and length, \(L\), 50mm and 100mm. The specific dimensions for each specimen are listed in Table 6-1. The upper and lower surfaces of each specimen in contact with the loading platens were polished flat and parallel to within 0.013mm. The sample dimensions were originally selected due to the availability of numerical relations previously derived by He et al. (1995) for samples with similar dimensional ratios, using numerical simulations and linear elasticity. However, since the results of this model, as well as other published models that we examined, did not correlate with our experimental data, samples with other dimensions were produced and tested in order to identify potential sources of the discrepancy.
Table 6-1. Specimen dimensions.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>L (mm)</th>
<th>2w (mm)</th>
<th>t (mm)</th>
<th>R (mm)</th>
<th>w/R</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>8</td>
<td>11</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>8</td>
<td>11</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>8</td>
<td>11</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>8</td>
<td>11</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>8</td>
<td>11</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>8</td>
<td>11</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>8</td>
<td>11</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>12</td>
<td>11</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>100</td>
<td>12</td>
<td>11</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>12</td>
<td>11</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>11</td>
<td>50</td>
<td>12</td>
<td>11</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>12</td>
<td>50</td>
<td>12</td>
<td>11</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>13</td>
<td>50</td>
<td>12</td>
<td>11</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>14</td>
<td>50</td>
<td>12</td>
<td>11</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

Previous work in this area indicated difficulty in growing stable cracks in PMMA using the DCDC sample geometry (Idonije et al. 1993; Jenne et al. 2003). In other materials, such as glass, it is often reported that the crack initiates at the crowns of the hole without the presence of a starter notch (Janssen 1974; Michalske and Fuller 1985; Crichton et al. 1999), while in polymers such as PMMA, a starter notch is necessary to initiate cracking at the crowns. Various schemes were undertaken in an effort to initiate a stable crack. Samples were notched along the entire length of the upper and lower crowns of the hole with a 0.2mm diamond wire saw. Likewise samples were scored along the entire length of the upper and lower crowns with a razor blade. A combination of these two methods was also attempted, where the crowns were notched through the sample thickness with the wire saw and subsequently scored with a razor blade. In each case a crack propagated from the upper and lower crowns, though the crack growth was highly unstable and resulted in
the crack extending rapidly to the far extremes of the sample length, similar to
previous experiments by Idonije et al. (1993).

A successful method was developed, however, by wedging a razor blade into
the material to create an actual crack, rather than a scratch or notch, at the crowns of
the hole. A curved blade was fixed in an end-mill and positioned above the sample
such that it extended beyond the diameter of the hole by 0.25mm. The blade was
pressed into the hole to a depth of about 1mm at the upper and lower crown of the hole
for both the front and back surfaces of the specimen. This method was successful in
wedging open and propagating a crack, though this could only be achieved close to the
surface of the specimen; see Figure 6-1. Hence the pre-crack was not continuous
through the thickness of the sample. However, during each test, as load was gradually
applied to the specimen, the crack would first grow through the thickness of the
sample until it formed a continuous crack front through the thickness of the specimen.
It would then grow towards the direction of the applied compression in a stable
manner. This would happen at both pre-notched crowns of the hole.

Samples were loaded quasi-statically in an Instron Model 1332 universal
testing machine in displacement control with an 88 kN load cell. An external camera
(Nikon D100) was focused at 4x magnification on the specimen. Each sample was
compressed at a rate of 1.3μm/s. The test was paused every 25μm in displacement,
for a duration of about 10 seconds, so that the peak load over that period could be
recorded along with a picture. The extended pause was implemented to ensure the
crack propagation had equilibrated prior to each photo. The crack length in each photo was later measured graphically by pixel counting software and correlated to the applied load.

6.3 Experimental Results

The typical compression test proceeded in the following way: after an initial buildup of strain within the specimen, the pre-crack would grow through the thickness to form a uniform crack front; the crack front would then grow in linear relation with the applied load and in a stable manner such that multiple data points could be obtained. This relation would taper off at some plateau stress whereby the crack would grow rapidly with little additional applied stress. In the stable region, there was little crack-opening displacement across the width of the sample. Upon reaching the plateau stress, the sample would bend outward due to the presence of a non-uniform stress distribution over the narrowest cross-section of the beam, resulting in a diamond shaped opening. The picture sequence in Figure 6-2 illustrates the propagation in a typical sample.

The crack front was observed to grow in a characteristic parabola shape similar to that observed in other DCDC experiments, indicative of the transition from plane strain at the center to plane stress at the faces (Janssen 1974). The crack length, \( l \), was measured from the top of the hole to the maximum extent of the crack in the direction of the applied compression, which was conveniently facilitated by the transparent nature of PMMA. The initial pre-cracks at the crowns of the hole were less than 1mm
in length. Crack length measurements were recorded only when the two starter cracks on the front and back faces had joined up and the parabolic crack front was observed. This shape was evident by the time the crack had reached a length of about 2 mm. The crack length, \( l \), was recorded as the average of the top and bottom crack lengths for each photo, typically within a few percent of each other over the course of the experiment.
Figure 6-2. Picture sequence, from left to right, top to bottom, of advancing crack. The lower left shows the sample loaded well into the plateau regime. Sample is viewed from same perspective as shown in Figure 6-1.
Crack propagation was more controllable and the results more repeatable for specimens with larger \( w/R \) ratio. For samples with \( w/R \) of 2, the crack would grow to a length of about 2mm and then rapidly extend to the full length of the sample. Samples with a \( w/R \) of 3, 4 and 5 exhibited stable crack growth over a greater range. Beyond a critical load, however, the crack would also grow rapidly. Samples with \( w/R \) of 5 demonstrated the most stable and repeatable crack growth. The results for all tests are shown in Figure 6-3 and Figure 6-4, in terms of applied stress versus normalized crack length.

For \( w/R \) ratios 2, 3 and 4, two different sample lengths (50mm and 100mm) were investigated. Long samples with a \( w/R \) ratio of 5 could not be tested due to buckling induced by the increased stress required to drive the crack in this geometry. Sample length had an effect on the results, where the longer samples required less stress to reach the plateau region. This effect is most evident in the results for samples with \( w/R \) of 4, where the plateau region of longer samples 17, 18 and 19 was less than the shorter specimen 20-24. This is attributed to friction at the sample ends in contact with the loading platens that acts to confine the sample laterally and oppose the crack opening tensile force. In the longer samples this confining force is located further from the crack front and thus has less effect compared to the shorter samples. To verify this, we performed a single test (specimen 28) where the platen surfaces were coated with a thin layer of lubricating grease to reduce the friction. As expected, the sample reached the plateau region at a lower applied stress compared to the results from otherwise identical specimens 25, 26 and 27. The effect of relative sample width
and hole diameter was shown to have no significant effect. The sample width and hole diameter were increased proportionately in samples 15 and 16 compared to samples 8, 9, and 10, such that a $w/R$ ratio of 3 was maintained in all specimen. The results for these tests fell within the experimental fluctuation for this $w/R$ ratio such that no difference was observed.

Figure 6-3. Experimental data for specimens with $w/R$ ratios 2 and 4.
6.4 Photoelastic Observation of DCDC Specimen

During crack propagation in the DCDC compression test, the sample will tend to deflect away from the crack plane when the crack extends beyond a certain length, defined by the plateau regime. When the crack extends into this region, plastic deformation may be introduced into the specimen, which can lead to residual strains when the axial compressive force is removed and the crack plane is brought back together. These strains will act to reduce the force required to re-open the crack thus influencing the evaluation of healing efficiency for that specimen. For this reason, crack healing measurements with the DCDC geometry should be carried out such that the crack is not extended beyond the plateau region.
As a means of visualizing the residual strains at progressive stages in the crack extension, a DCDC specimen of PMMA was viewed through crossed polars during axial compression. PMMA exhibits the property of birefringence under applied stress to visualize the stress within the material and is widely used in the study of photoelasticity (Coker and Filon 1931). The sample is placed between two polarizers and is illuminated with white light. Light passing through the first polarizer is linearly polarized and, upon entering the birefringent material, experiences different refractive indices and results in a phase difference between the waves. When the waves recombine in the second polarizer, color is observed if the waves are in phase; otherwise no color is observed. The level of birefringence in the sample depends on the stress level and thus highly stress areas will appear in a different color.

A DCDC specimen with \( w/R \) ratio 3 was machined from PMMA. The sample had flaws from machining that caused it to be rejected from quantitative evaluation of the stress vs. crack length experiments as discussed the previous section. Its ends were not planar and the precracks formed by the razor wedging process were not parallel. However these flaws provided an interesting demonstration on the effect of the symmetric distribution of stress within the specimen when viewed through crossed polarized lenses.

Figure 6-5 illustrates the distribution of stress within the sample during increasing axial compression. Photographs were taken while the sample was under compression. It should be noted that the light used to illuminate the sample was
positioned behind the specimen, slightly towards the right side (when facing the specimen), which caused the intense white region visible on that side in the photos.

A stress concentration visible in the upper right hand corner of the specimen is due to a non-planar surface (high point) on the upper surface. This asymmetry likely contributed to the unequal lengths of the crack viewed in the last photo. Moreover both cracks appear to have veered slightly off center.
Figure 6-5. Stress distribution during crack propagation in PMMA specimen under increasing axial compression (left to right, top to bottom).

At various stages during the progression of the crack, the load was removed and the sample again photographed. Birefringence in these photographs is caused by
residual strain in the sample as a result of plastic deformation. The sequence of photos for the uncompressed specimen is given in Figure 6-6.

The first photo on the left also shows residual stress around the hole as a result of the machining process. This specimen was fabricated by laser machining, which may introduce a greater heat affected zone than traditional milling and drilling. The color around the hole does not appear to change significantly until the third photo from the left. This change in color may be interpreted as residual strain in the sample due to inelastic deformation. At this point the crack has extended to a length that falls within the plateau regime for PMMA in that DCDC geometry (Figure 6-7). These photos demonstrate that while the crack length is less than the radius of the hole, the sample is largely free of inelastic deformation.
Figure 6-7. Model for DCDC specimen with \( w/R \) ratio of 3. The end of the stable crack growth occurs roughly when the crack has reached length equivalent to the radius of the hole (\( \lambda \equiv 1 \)).

### 6.5 Modeling

In this section we develop a simple yet accurate analytical model for describing the propagation of a crack in a polymer DCDC specimen under uniaxial compression. The calculations are straightforward and do not require the finite-element simulations that have recently been used by Jenne, et al. (2003). The model reproduces the experimental results more accurately than any of the other published models that we have sought to use, e.g., (Sammis and Ashby 1986; He et al. 1995; Jenne et al. 2003). Some possible causes of this are examined at the end of the chapter.
To simplify the modeling, we consider two extreme cases: a short-crack regime and a long-crack regime. In the DCDC test, the normal stress required to extend the crack increases with the crack length in the short-crack regime, whereas a load plateau exists in the long-crack regime with little additional stress being required to substantially increase the crack length. The onset of this plateau designates the boundary between the “short” and “long” crack regimes. There is of course a small transition regime that we do not address in our modeling.

To model the short-crack, first consider the Green's function for a slit crack in an infinite plate subjected to two pairs of concentrated forces, as shown in Figure 6-8. The resulting stress intensity factor is (Erdogan 1962),

$$K = \frac{P}{\sqrt{\pi a}} \left( \sqrt{\frac{a + x}{a - x}} + \sqrt{\frac{a - x}{a + x}} \right).$$  \hspace{1cm} \text{Equation 6-1}

Then note that, in the absence of cracks, a hole in an infinite plate subjected to axial compression induces the following tensile stresses over the interval $R < |x| < R\sqrt{3}$ on the plane $y = 0$:

$$\sigma_{yy}(x) = \sigma_a \left( -\frac{1}{2(x/R)^3} + \frac{3}{2(x/R)^4} \right).$$  \hspace{1cm} \text{Equation 6-2}

Here $\sigma_a$ denotes the applied axial stress. In what follows, we identify $\sigma_a$ with the applied axial load when the crack length is $l$, and, for this reason, henceforth we denote $\sigma_a$ by $\sigma_a(l)$. The stress intensity factor at the tip of a slit crack of length $2(l +
$R$) in an infinite plate, subjected to internal opening stresses $\sigma_{yy}(x)$ over the interval $R < |x| < R\sqrt{3}$, is

$$K = \int_{R}^{R\sqrt{3}} \frac{\sigma_{yy}(x)}{\sqrt{\pi(l+R)}} \left( \frac{l+R+x}{l+R-x} + \frac{l+R-x}{l+R+x} \right) dx$$

Equation 6-3

$$= \frac{\sigma_0(l)\sqrt{R}}{\sqrt{\pi(1+\lambda)}} \int_{0}^{1} \left( - \frac{1}{2\xi^2} + \frac{3}{2\xi^4} \right) \left( \frac{1+\lambda+\xi}{1+\lambda-\xi} + \frac{1+\lambda-\xi}{1+\lambda+\xi} \right) d\xi.$$ 

Here $\lambda = l/R$. The integral can be evaluated numerically. Note that for $l > R\sqrt{3}$, $\sigma_{yy}(x)$ is compressive, and hence does not affect the stress intensity factor. A good approximation is achieved by replacing the stress distribution with an equivalent concentrated force, $P$, acting at a distance $x$,

$$P = Rd\sigma_x(l),$$

Equation 6-4

$$x = eR$$

Equation 6-5

The magnitude, $P$, and the point of the application, $x$, of this force are estimated by integrating the stress distribution in (Equation 6-2). This gives,

$$d = \frac{\sqrt{3}}{9} \sim 0.19254,$$

Equation 6-6

$$e = \frac{3\sqrt{3}}{4}(2 - \ln 3) \sim 1.1709.$$ 

Equation 6-7

The stress intensity factor due to this concentrated force is a very good approximation of Equation 6-3. It yields,

$$K = \frac{d\sigma_0(l)\sqrt{R}}{\sqrt{\pi(1+\lambda)}} \left( \frac{1+\lambda+e}{1+\lambda-e} + \frac{1+\lambda-e}{1+\lambda+e} \right).$$

Equation 6-8
Comparison between this and the more complicated form (Equation 6-3) shows little deviation. The non-dimensional version of this equation is,

\[
\frac{\sigma_0(l)\sqrt{w}}{K_c} = \sqrt{\frac{w}{R}} \sqrt{\pi(1+\lambda)} \cdot d \left( \frac{1+\lambda+e}{\sqrt{1+\lambda-e} + \sqrt{1+\lambda+e}} \right)
\]  

Equation 6-9

We now seek to modify and apply this equation to the actual problem shown in Figure 6-9, where relatively short cracks extend from the crowns of a circular hole in a beam of finite width, 2w, under axial compression. To account for the effect of the finite width, we now view the parameter d as a scaling factor and allow it to be a function of w/R. When the ratio w/R becomes very large, the value of d(w/R) is expected to approach that of Equation 6-6, calculated based on the Green’s function of an unbounded medium. As the values of w/R decreases, we expect the value of d(w/R) to increase since the presence of the hole in a finite-width sample promotes crack growth under axial compression. Equivalently, the stress intensity factor at the crack tip will tend to be larger. For an average critical stress intensity factor of 
\[K_{IC} = 0.71 MPa\sqrt{m}\], calculated from the long-crack model (discussed below), the normalized values of d(w/R) with respect to the theoretical value of Equation 6-6 for an infinite plate shown in Figure 6-10 reproduce the experimental results with small error, up to the point where the axial stress approaches the limiting value of the long-crack model. As expected, d(w/R) is a monotonically decreasing function of w/R, approaching unity in the limit of very large w/R. Since we are concerned with
relatively small values of \( w/R \) associated with our beam-column samples, we may use a linear fit within the considered range, arriving at,

\[
\frac{d(w/R)}{d_\infty} = 5.7 - 0.75 \frac{w}{R}.
\]  

Equation 6-10

Note that this fit is only useful for the range of geometries studied here.

Figure 6-8. Representation of a slit crack with symmetric concentrated loads.

Figure 6-9. Schematics and dimensions of the DCDC model.
Figure 6-10. Normalized values of \( d(w/R) \) with respect to the theoretical prediction in an infinite plate.

When the crack is suitably long, we use an Euler-Bernoulli beam model with appropriate boundary conditions applied to one quarter of the sample. The deflection of the beam is defined by the following boundary-value problem:

\[
\frac{d^2}{dx^2} \left( EI \frac{d^2 v}{dx^2} \right) = 0, \quad \text{Equation 6-11}
\]

\[ v(x = l + R) = 0, \quad \text{Equation 6-12} \]

\[ \frac{dv}{dx} (x = l + R) = 0, \quad \text{Equation 6-13} \]

\[ \frac{dv}{dx} (x = 0) = 0, \quad \text{Equation 6-14} \]

\[ EI \frac{d^2 v}{dx^2} (x = 0) = M_0. \quad \text{Equation 6-15} \]
Here \( \nu(x) \) is the deflection of the beam at point \( x \), measured normal to the axis of the beam; \( E \) is the Young’s modulus of the sample; \( I \) is the area moment of inertia of the cross-section; and \( M_0 \) is the moment induced at the end of the beam due to the non-uniform axial stress distribution at \( x = 0 \), over the section \( R < y < w \). Since the beam is long relative to the hole radius, we take \( I \) to be constant throughout the entire length of the beam, ignoring the reduced cross-section at the hole, \( i.e., \) we set \( I = bw^3/12 \), where \( b \) is the sample thickness. The resulting bending moment in the beam is,

\[
M(x; l) = EI \frac{d^2 \nu}{dx^2}(x) = M_0(1 - 2 \frac{x}{l + R}),
\]

Equation 6-16

and the bending energy, the resulting energy release rate (per unit area), and the stress intensity factor respectively become,

\[
E(l) = \int_0^{x_R} \left[ M(x; l) \right]^2 \frac{dx}{2Elb},
\]

Equation 6-17

\[
G(l) = 2 \frac{\partial E}{\partial l},
\]

Equation 6-18

\[
K = \sqrt{EG} = \frac{2M_0}{bw^{3/2}}.
\]

Equation 6-19

The factor 2 appears in Equation 6-18 since we have considered one quarter of the sample when there are actually two beams contributing to the energy release rate at the crack tip.
Note that, in this regime, $M_0$ does not change as the crack grows. As the beam deforms under the axial compression, the bending moment at the end of the beam does not change with the increasing deflection. When the crack length is large compared to the hole radius and the width of the sample, $l/R >> 1$ and $l/w >> 1$, the stress field at the crack tip does not change with crack growth. Since $M_0$ depends on the ratio $w/R$, to apply the results to samples with various $w/R$, we now express this bending moment in terms of a non-dimensional function, $g(w/R)$, as follows:

$$M_0(R, w) = \sigma_p bwR g(w/R).$$  \hspace{1cm} \text{Equation 6-20}$$

Here $\sigma_p$ is the axial stress applied to the sample in the plateau regime. The plateau stress and the critical stress intensity factor are related by,

$$\frac{\sigma_p \sqrt{w}}{K_c} = \frac{w/R}{2g(w/R)}.$$  \hspace{1cm} \text{Equation 6-21}$$

To calculate the function $g$, we assume that the axial stress on the plane $x = 0$ consists of two parts, as follows:

$$\sigma_{xx}(y) = -\sigma_p \left[ \left( 1 + \frac{1}{2(y/R)^2} + \frac{3}{2(y/R)^4} \right) \frac{(\alpha w - \beta R) + (\beta - \alpha) y}{w - R} \right].$$  \hspace{1cm} \text{Equation 6-22}$$

The first part corresponds to the terms inside the parentheses within the brackets on the right-hand side. It represents the compressive stresses transmitted on the plane $x = 0$ near a hole in an infinite plate. The second part is the last term within the brackets, and corresponds to a superposed linear stress distribution. We determine the parameters $\alpha$ and $\beta$ such that the resultant moment due to this term, taken about the
neutral axis \( y = w/2 \), is zero. This condition together with the requirement of axial equilibrium, yields the following expressions for these parameters:

\[
\alpha = \frac{(R/w)^2(1 + (R/w)^2)(4(R/w) - 1)}{(1 - R/w)^2},
\]

Equation 6-23

\[
\beta = \frac{(R/w)^2(1 + (R/w)^2)(2(R/w) + 1)}{(1 - R/w)^2}.
\]

Equation 6-24

Calculating the bending moment about the neutral axis, \( y = w/2 \), we obtain the function \( g(w/R) \),

\[
g(w/R) = \frac{3 + 2\ln(w/R)}{4(w/R)} = \frac{1}{4(w/R)^2}.
\]

Equation 6-25

Equation 6-21 and Equation 6-25 now give the final model estimate of the normalized axial stress corresponding to the plateau stress for samples of various geometries. Using the experimental results when the crack is suitably long, we have obtained an average value for the critical stress intensity factor for this material, \( i.e., \)

\( K_{IC} = 0.71 \text{MPa}\sqrt{m} \). The value of the critical stress intensity factor obtained in this manner for all our tests lies within 10% of this value and well within the range of critical stress intensity factors given in the literature for PMMA (Marshall and Williams 1973). In Figure 6-11 we have plotted the product of the plateau stress and \( w^{1/2} \) versus the \( w/R \) ratio, for \( K_{IC} = 0.71, 0.64, 0.78 \text{MPa}\sqrt{m} \), \( i.e., \) the average (solid curve) and the average plus and minus 10% (dashed curves). The model estimates closely follow the experimental results for all test geometries. Figure 6-12 and Figure 6-13 compare the short- and long-crack model results with the experimental data.
Figure 6-11. Plateau stress versus $w/R$ ratio. The circles are the experimentally measured values. The solid curve represents the model result for a critical stress intensity factor of $K_{IC} = 0.71MPa\sqrt{m}$, while the dashed curves are for a 10% variation, i.e., $K_{IC} = 0.64, 0.78MPa\sqrt{m}$. 
Figure 6-12. Axial load versus normalized crack length for \( w/R = 2 \) and 4: The solid and dashed curves represent the model results for the indicated values of \( w/R \), using the critical stress intensity factors \( K_{IC} = 0.71 \text{MPa}\sqrt{m} \) and \( K_{IC} = 0.64, 0.78 \text{MPa}\sqrt{m} \). The initial curved segment is the short-crack solution and the flat line is the asymptotic long-crack solution.
Figure 6-13. Axial load versus normalized crack length for $w/R=3$ and $5$: The solid and dashed curves represent the model results for the indicated values of $w/R$, using the critical stress intensity factors $K_{IC} = 0.71 \text{MPa}\sqrt{m}$ and $K_{IC} = 0.64, 0.78 \text{MPa}\sqrt{m}$. The initial curved segment is the short-crack solution and the flat line is the asymptotic long-crack solution.

### 6.6 Discussion

Here we compare our experimental and analytical results with other published work. We focus on Michalske et al. (1993) and He et al. (1995), but the following comments apply also to all the models based on linear elasticity and linear finite-element solutions. In the present case, linear elasticity predicts a monotonically decreasing stress intensity factor at the tip of the crack as the crack length $l$ increases, thus requiring a monotonically increasing axial compression to drive the crack in a
material with a constant critical value of the stress intensity factor. Using linearly elastic finite-element numerical simulations, He et al. (1995) for example find a linear relation between the (normalized) required axial stress and the (normalized) crack length. An examination of Figure 6 in this publication shows a stress distribution around the hole that produces a (normalized) bending moment, taken about the neutral axis of the beam, which decreases by a factor of 8 when the crack length changes from \(a/R=2\) to \(a/R=14\); we have used a similar finite-element calculation to confirm this trend.

However, in a beam with a central hole under axial compression, the lateral deflection at the hole produces an effective bending moment that cannot be captured by the infinitesimal deformation assumed in linear elasticity since the deflection is a second-order quantity. For very stiff materials, this lateral deflection is very small, as may have been the case in the works of Michalske et al. (1993) and Turner et al. (1995), yet should have become evident had the crack been further extended in a sufficiently long sample. Michalske et al. (1993) tested fused silica \((E=94\text{GPa}, K_{IC}=0.74\text{MPa}\sqrt{m})\) in ultra high vacuum and incrementally extended the crack by superimposing short duration stress pulses on a constant axial stress of sufficiently small value that would not extend the crack in the absence of the impulse. Turner et al. (1995) examined interface crack growth in a glass-epoxy-glass specimen \((\Gamma_{IC}=24J/m^2, K_{IC}=1.29\text{MPa}\sqrt{m})\), using soda-lime glass \((E=69\text{GPa})\). They also examined interface crack growth in a sapphire-gold-sapphire specimen.
(\(\Gamma_c = 10J / m^2, K_{IC} = 1.97 \text{MPa}\sqrt{m}\)), and a sapphire-platinum-sapphire specimen
(\(\Gamma_c = 30 - 52J / m^2, K_{IC} = 3.42 - 4.5 \text{MPa}\sqrt{m}\)), with sapphire having a Young's modulus of \(E=390\text{GPa}\). Like our experiments, the load was monotonically increased after an initial pre-crack had been established. The materials tested in these experiments were comparatively stiff with low interface fracture toughness, which masked the second-order effects evident in our experiments.

In our beam-column analysis, we have assumed, for a sufficiently long crack, that the presence of the hole creates a bending moment on the cross-section at \(x = 0\) (i.e., at the hole) that is not affected by the crack length. With this assumption, we have shown that the beam-column model, based on a strength-of-material approach, does indeed produce results that are in accord with the experimental data, using a constant value for the critical stress intensity factor that is within the expected range, hence suggesting that this simple model includes the essential physical features necessary to capture the essence of the experiments. Alternatively, one may consider a beam-column boundary-value problem and obtain a more accurate expression for the bending moment, as follows:

\[
M(x) = M_o (\cos qx - \frac{\sin ql}{1 - \cos ql} \sin qx),
\]

Equation 6-26

where \(q^2=P/EI\). This gives a stress intensity factor of

\[
K = \frac{2\sqrt{3}M_o}{bw^{3/2}} \sqrt{1 - \frac{\sin ql(ql - \sin ql)}{(1 - \cos ql)^2}},
\]

Equation 6-27
which, similar to the previous results, is a very slowly varying function of $l$ for $ql<1/3$. In fact, for $ql=1/3$ (less than the largest value of the corresponding quantity in our experiments), Equation 6-27 is to within 1% of (19). Furthermore, $K(l)$ in Equation 6-27 is a very slowly increasing function of the crack length, which demonstrates the stability of the crack growth, as has been observed in our experiments; this may be partially evident in Figure 6-3 and Figure 6-4 that show, for most experiments, very slightly increasing fracture stress with increasing crack length, in the plateau regime; this may be more evident for data in Figure 6-12 corresponding to $w/R = 4$. The moment distribution and related deformation also show that the deflection around the hole is a local phenomenon and does not change when the crack length is increased, suggesting that the constant moment assumption is validated. An extended analysis by Jenne et al. (2003) uses a similar approach, based on the work by Sammis and Ashby (1986). Sammis and Ashby use a strength-of-material approach to study the effect on a plate's compressive uniaxial stress-strain relation, due to axial cracks that emanate from the crowns of circular holes that are periodically distributed in an infinite linearly elastic plate. Their calculations however are flawed by the incorrect estimate of an integral, for which they assume that the crack length is infinitesimally small relative to the radius of the hole and then apply the results to cases where the crack length exceeds ten times the hole radius. Remarkably, this error leads to results that nicely correlate with the experimental observations on rock failure, but unfortunately does not follow from the correct solution of their model. This has been pointed out by Isida and Nemat-Nasser (1987) who provide the correct elasticity solution which shows that the common length of the axial cracks in such situations (infinite linearly elastic plate
with periodic hole-crack distribution) has only a second-order effect on the axial stress-strain relation and hence it can have no relation to the experimental results on rock failure in compression.

6.7 Conclusions

Fracture studies of brittle polymer PMMA have been conducted using DCDC specimens. Pre-cracking and loading procedures were developed to propagate a stable crack from the upper and lower crowns of a central hole in a beam of rectangular cross-section subjected to axial compression. Stable crack growth was achieved until a plateau stress was reached, at which stage the resulting bending moment caused the crack to grow rapidly. The test results were modeled using expressions reported in the literature, but discovered that none of the published models produced results in accord with our experimental data. Thus, a simple model was developed that combines a suitably modified version of two estimates, one based on a short-crack and the other on a long-crack approximation. This model produces results in good accord with all our experimental results and also yields a reasonable value for the fracture toughness of the material. The published models based on finite-element linear elasticity solutions were deemed inappropriate tools for solving the present problem, since linear elasticity cannot capture the second-order effect due to the rotation of the cross-section of the beam, which is crucial to the correct estimate of a beam-column response.
6.8 Acknowledgement

Portions of this chapter were published in the *International Journal of Fracture* in October 2006, entitled “Compression-induced axial crack propagation in DCDC polymer samples: experiments and modeling”. The dissertation author was the primary investigator and author in this publication. Co-authors Alireza Amirkhizi and Sia Nemat-Nasser are thanked for their contributions to the modeling portion of this work.
Quantitative Evaluation of Fracture, Healing and Re-healing of a Reversibly Cross-linked Polymer

This chapter describes the results of repeated fracture-healing characteristics of 2MEP4F polymer using the DCDC geometry. This method allows for systematic and quantitative evaluation with controlled incremental crack growth so that the cracked sample remains in one piece after the test, improving the ability to re-align the fracture surfaces prior to healing. The specimens have been pre-cracked to a repeatable length to enable accurate comparison between virgin and healed fracture loads, and hence fracture toughness. Moreover, multiple data points are extracted from a single sample. Results are presented that demonstrate healing at temperatures between 85 to 95°C, after repeated fracture-healing cycles, results in full fracture toughness recovery and no dimensional changes due to creep. The fracture toughness after each fracturing and healing cycle has been calculated, using a model developed and tested in Plaisted et al. (2006), arriving at consistent results for repeatedly healed 2MEP4F polymer. These results show a fracture toughness of about 0.71 MPa·m$^{1/2}$ for this material at room temperature. Healing for shorter periods, as little as 30 minutes, using the same temperature-pressure cycle, has yielded essentially the same final results, i.e., full toughness recovery. That the healing process is largely independent of time is in contrast to the diffusion-controlled healing observed in the welding of thermoplastics polymers. Rather, it shows that the healing in the 2MEP4F polymer results from the repair of the broken Diels-Alder (cross-linking) bonds that seems to restore a
molecular structure similar to that of the original virgin polymer with the same (or even slightly improved) overall macroscopic fracture resistance.

### 7.1 Introduction

A material that can heal itself is of great utility where access for manual repair is limited or impossible, as in a biological implant or a material that is launched into orbit in outer space. Structures made of such materials may have significantly prolonged service life in addition to improved safety if failure in the form of cracking can be repaired in-situ. Nature has long demonstrated this property in various biological materials, whereas, until recently, man-made healable materials have essentially not been demonstrated. Recently, interest in synthetic healable materials has gained some attention with the creation of an autonomic healable polymer by White et al. (2001). In this system, microencapsulated liquid monomer is embedded with dispersed catalyst in a thermoset polymer, such that a propagating crack that intersects and fractures the microcapsules causes a release of the healing agent to fill and effectively glue the faces of the crack back together. An alternate approach to healing is to develop a polymer with the ability to repair internal cracks by using a thermally-reversible Diels-Alder (DA) and retro-DA cycloaddition. Many polymers involving the DA cycloaddition have been synthesized, though in many cases the retro-DA reaction is not observed if the diene and dieneophile are not sufficiently stable on their own. Those polymers with suitable monomer combinations to exhibit the retro-DA reaction have incorporated the DA adduct into the backbone of the polymer (Chujo et al. 1990; Engle and Wagener 1993; Imai et al. 2000). Recently,
Chen et al. (2002; 2003) have succeeded in creating healable polymers such that all of the monomer linkages, or cross-links, are formed by DA cycloaddition and furthermore, by careful design of the monomers, exhibit the retro-DA reaction.

![Figure 7-1](image)

Figure 7-1. The healable polymer consists of a multifuran molecule combined in stoichiometric ratio with a multimaleimide molecule to form 2MEP4F cycloadduct.

The repair mechanism of these polymers relies on a Diels-Alder (DA) bond, as illustrated in Figure 7-1 for 2MEP4F polymer. This covalent bond is weaker than other bonds in the polymer backbone, so that, when the sample is loaded excessively, it will break preferentially along these bonds as compared to the other covalent bonds in the molecule. Chen et al. previously reported the bond energy of the DA adduct to be about 23 kcal/mol by measuring the exotherm during polymerization of similar maleimide and furan monomers (Chen et al. 2002). Above ~110°C, the bonds will also disconnect (retro-DA cycloaddition) such that approximately 12% disconnect after 25 minutes at 130°C for 3M4F polymer (Chen et al. 2003). Below 110°C, the
stable state of the DA moieties is to re-connect as a cycloadduct. Thus, healing is achieved by bringing the broken DA moieties into proximity of one another at a temperature below 110°C. This suggests that macrocracks in the polymer can be healed by bringing the fractured interfaces together through pressure at suitable temperatures to accelerate healing while avoiding creep, and then cooling the polymer to room temperature. Heating provides sufficient conformational motion in the polymer structure to bring the de-bonded maleimide and furan groups into close proximity. In theory, the bond will self-repair at any temperature below the retro-DA temperature (110°C) provided that the broken moieties come into contact.

Figure 7-2. Dynamic Mechanical Analysis of 2MEP4F polymer cycled at 1Hz and heated at 3°C/min.
Repair of a significant fraction of the broken cross-links should lead to a commensurate recovery of the polymer's macroscopic fracture strength (e.g., the energy-release rate, or equivalently, the fracture toughness). The macroscopic toughness of the polymer stems from the energy loss due to various micro- and macro-mechanisms that are activated during bond breaking, which generally by itself contributes only a small fraction of the total energy loss (measured per unit fracture-surface area) (Andrews and Stevenson 1978; King and Andrews 1978; Kinloch and Young 1983; Robertson et al. 1989). Thus, the efficiency of the polymer's fracture toughness recovery (a macroscopic effect) is directly dependent on its efficiency to recover (heal) its broken DA cross-links.

The healing efficiencies of 3M4F and 2MEP4F polymers have been previously quantified using compact tension specimens with and without a crack-arresting central hole (Chen et al. 2002; Chen et al. 2003). For 3M4F polymer, Chen et al. report healing at 150°C with 50% efficiency and at 120°C with 41% efficiency, although the sample fractured into two which precluded suitably accurate realignment of the fracture interfaces prior to healing (Chen et al. 2002). These temperatures seem too high considering that dissociation of the DA bonds takes place to such an extent that at 150°C the polymer essentially can be remolded into a new configuration. In the case of 2MEP4F polymer, a specimen with a crack-arresting hole was used and the fracture stopped at the hole (Chen et al. 2003). The sample was then clamped and healed at 115°C for 30 minutes. The pressure applied by this clamp was not quantified. Upon re-testing, the specimen fractured at an average of 78% of the original fracture load.
At 115°C, this polymer has an insignificantly small storage modulus, as shown in Figure 7-2 and also in Figure 4b of Chen et al. (2003).

The following experiments seek to examine the repeated fracture-healing characteristics of the 2MEP4F polymer in a systematic and quantitative manner, using a sample geometry and relative dimensions that allow for controlled incremental crack growth while minimizing any potential inelastic deformation away from the crack tips. In the fracture mechanics literature, this sample is called the *Double Cleavage Drilled Compression* (DCDC) specimen, which is a relatively long column of rectangular cross-section that contains a through-the-thickness central, circular hole with small notches at its axial crowns. Under an increasing uniform axial compression, cracks initiate at the crowns and grow axially in a stable manner, along the mid-plane of the sample. By careful displacement-controlled loading, the crack growth can be controlled to a certain extent. A unique property of this specimen geometry is that it renders the cracks self-arresting so that the fractured sample remains in one piece after the test, which greatly improves our ability to re-align the fracture surfaces prior to healing. The sample may also be pre-cracked to a repeatable length to allow for a more accurate comparison between virgin and healed fracture loads, and, hence, fracture toughness. Moreover, multiple data points can be extracted from a single sample, making it well suited for quantifying the material's fracture toughness after several fracturing and healing cycles. To test the viability of this method, control of the fracture process was verified using a number of samples made from poly(methymethacrylate), arriving at remarkably consistent results; see Plaisted et al.
In addition, based on these experiments, the relative dimensions (see Table 7-1) of the 2MEP4F samples were selected such as to allow for a direct measurement of the room-temperature, quasi-static fracture toughness without introducing unwanted inelastic deformations elsewhere within the specimen.

Initial experiments on 2MEP4F samples were focused on the investigation of the healing efficiency reported previously by Chen et al. (2003) for 2MEP4F polymer, attempting to duplicate the same treatment conditions as used in those experiments to induce healing, but using the DCDC sample geometry. To this end, a DCDC specimen of 2MEP4F polymer was fractured as previously described. The fractured sample was immediately placed inside an oven pre-heated to 115°C, within a fixture that consisted of two flat surfaces lined with PTFE film, and loaded on the top surface such that a uniform pressure of 0.035 MPa was exerted normal to the crack interface. Two thermocouples were placed in close proximity to the sample to monitor the temperature of the sample and as a secondary measure of the oven’s internal thermocouple. After 30 minutes the sample was cooled to room temperature over the course of six hours. Upon removing from the fixture, it was evident that the sample had undergone significant creep, to the point that the 4mm central hole was no longer visible. Although the crack had likewise disappeared, the sample could no longer be tested.

The same experiment was repeated on another specimen; however in this case no pressure was applied. The only load acting upon the sample was that of its own
weight, oriented such that the crack interface was parallel to the surface on which the sample was resting. After the thermal treatment, as described above, the sample again had deformed due to creep. The resulting change in geometry made comparison between the virgin fracture event and successive fracture events impossible.

In this chapter, results of repeated fracturing and healing cycles are reported, where the DCDC sample geometry is utilized and healing is activated at moderate thermal treatment temperatures. Healing at temperatures in the range of 85 to 95°C, after repeated fracture-healing cycles, results in full fracture toughness recovery. The fracture toughness after each fracturing and healing cycle is calculated, using a model developed and tested in Plaisted et al. (2006), arriving at reasonably consistent results for repeatedly healed 2MEP4F polymer.

### 7.2 Sample Fabrication

Bismaleimide (2MEP) and tetrafuran (4F) monomers were prepared according to procedures outlined in the literature (Chen et al. 2002; Chen et al. 2003). Polymerization was carried out in the following way. Monomer 2MEP was heated above its melting point to a temperature of 95°C. Furan monomer 4F was likewise heated to 95°C to reduce its viscosity and the two monomers were combined in stoichiometric proportion and mixed under vacuum for about thirty seconds. Prior to gelation, the pre-polymer was poured into molds constructed of silicone in the rectangular shape of the DCDC specimen geometry and held at 100°C. A hard
polymer was formed within about 30 minutes at this temperature, though to ensure complete polymerization the samples were kept at this temperature for fifteen hours. The polymerized samples were then cooled to room temperature over a period of ten hours.

Four samples were machined to dimensions listed in Table 7-1 and labeled in Figure 7-4. The $w/R$ ratio, which influences the length over which the crack propagates in a stable manner, is about 4. We had already established that this relative dimension would also minimize possible inelastic deformations away from the crack tips (2006). The upper and lower surfaces of each specimen in contact with the loading platens were polished flat and parallel to within 0.013mm.

Table 7-1. Specimen dimensions.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$L$</th>
<th>$w$</th>
<th>$t$</th>
<th>$R$</th>
<th>$w/R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>7.8</td>
<td>8.8</td>
<td>1.98</td>
<td>3.95</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>7.8</td>
<td>8.3</td>
<td>1.98</td>
<td>3.95</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>7.8</td>
<td>8.2</td>
<td>1.98</td>
<td>3.95</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>7.8</td>
<td>9.3</td>
<td>1.98</td>
<td>3.95</td>
</tr>
</tbody>
</table>

7.3 Crack propagation and Experimental Procedure

The method to pre-crack the sample involved wedging a blade into the central hole of the DCDC geometry, following the procedure reported previously, to create sharp notches at the axial crowns of the hole on the front and back surfaces of the
A restraining clamp was then placed around the sample and compression was applied in the axial direction. The clamp provided lateral confinement which prevented the cracks from growing beyond a length, $l\approx 0.8$) from the crowns of the hole. Figure 7-3 illustrates the sample with confining clamp attached and the repeatable length to which the pre-cracks were propagated. Having introduced a uniform crack emanating from the upper and lower crowns of the hole, the clamp was removed and the specimen was then re-loaded in compression to record the force and crack length of the subsequent fracture event.

Figure 7-3. Lateral confining fixture attached to specimen to create pre-crack. Left – Specimen prior to axial compression with small razor notches visible at upper and lower crowns of central hole. Right – Application of axial compression initiates cracks which propagate from razor notches and are arrested at a length of ~1.8 mm, which forms the pre-existing crack for subsequent fracture-toughness measurement.

Samples were loaded quasi-statically in an MTS Model 244.12 universal testing machine in displacement control with a 25 kN load cell. An external camera (Nikon D100) was focused at 4X magnification on the specimen. Each sample was
compressed at a rate of 0.25 \( \mu \text{m/s} \). The test was paused at increments of 25\( \mu \text{m} \) in cross-head displacement, and after an equilibration period of about 10 seconds, the peak load over that period was recorded and a photo was taken. The crack length in each photo was later measured graphically by pixel counting software and correlated to the applied load. The crack length, \( l \), was recorded as the average of the top and bottom crack lengths from each photo, typically within a few percent of one another, over the course of the experiment. The error within the load and crack length measurements was sufficiently low that error bars are not visible on the scale of the figures as presented. 

The healing treatment consisted of the following procedure. Following the fracture event, the sample was immediately placed inside a pre-heated oven at the desired temperature. The sample was placed within a pre-heated vise with two parallel surfaces lined with PTFE film such that a uniform pressure was applied normal to the crack interface. The vise was tightened to a uniform torque with each healing treatment, which correlated to applying roughly 0.35 MPa normal to the crack plane. Two thermocouples were placed in close proximity of the sample to monitor the temperature of the sample and as a secondary measure of the oven’s internal thermocouple. The healing treatment was a two-stage process. The first stage consisted of heating the sample to 85\( ^\circ \text{C} \) while applying pressure with the vise to bring the crack faces into intimate contact. After a period of time under this treatment, the crack was no longer visible. The vise was then removed and the sample was further heated to 95\( ^\circ \text{C} \) for a period of time to maximize the mobility of the pendent furan and maleimide groups without inducing shape change (creep) in the sample.
The above healing procedure was derived from preliminary tests to determine the minimum treatment temperature at which the crack appeared to repair in a reasonable time period. At treatment temperatures below 80°C with applied pressure of 0.35 MPa there was little to no change in the crack interface after 3 hours. For treatment at 80°C to 82°C, the crack had partially disappeared. The areas towards the tips of the crack appeared to have been repaired, but the repair was less uniform towards the hole. When reloaded, the crack would re-open at a stress less than 10% of the stress required to extend the crack in the virgin specimen. For treatment in the range of 83°C to 85°C, the healing was more uniform, though the stress required to re-open the crack was no more than 50% of the original stress. When this sample was heated to between 85°C and 90°C under pressure of 0.35 MPa, slight creep was observed. It was concluded that 85°C was the maximum temperature at which the clamp pressure could be applied to the sample without inducing shape-changing creep.

In order to maximize the healing, a treatment method was proposed that would allow the crack interface to come back into intimate contact with applied pressure at the relatively low temperature, 85°C. Once intimate contact and partial healing had been attained, the pressure could be removed and the temperature elevated (to 95°C) to fully induce repair.
Figure 7-4. Top - Schematic of DCDC sample geometry. Dotted lines represent the location of the pre-crack and subsequent crack extension. Bottom - Fracture and healing sequence of a single sample. A) Virgin sample with hole and pre-cracks visible; B) Sample after first fracture event; C) Sample after first healing treatment; D) Sample after second fracture event.

The picture sequence for the fracture and healing of a single specimen is shown in Figure 7-4. After the first healing treatment, the crack largely disappears to
the naked eye. When re-fractured, the crack appears to propagate along the same path as the original crack. This fracture-healing process is carried out multiple times on the same sample.

When the applied stress exceeds the critical fracture stress, or equivalently when $K_I$ exceeds the $K_{IC}$ of the material, the crack will grow. The healing efficiency, $\eta$, is calculated as a ratio of the stress required to propagate the crack to a given length in the healed material to the stress required to propagate the crack to approximately the same length in the virgin material, expressed by:

$$\eta = \frac{\sigma_{crit}^{healed}}{\sigma_{crit}^{virgin}}$$

Equation 7-1

Due to the identical geometry of the sample before fracture and after healing, the critical fracture stresses may be directly compared. The lack of control inherent in the fracture process precludes comparison of identical crack lengths and associated stresses in the virgin and healed fracture events. Rather, we can only compare critical stress values for cracks of roughly equivalent length. Healing efficiencies are listed in tables for each specimen and indicate how close the crack length in the healed and virgin cases was in terms of a positive (longer than the virgin crack) or negative (shorter than the virgin crack) percentage. Typically the length of the crack in the healed case was slightly shorter than the virgin crack, and as such provided a conservative estimate of healing efficiency. Since the crack propagates and arrests
multiple times within one fracture cycle, the healing efficiency over that cycle may be averaged.

7.4 Experiments

Specimen 1

During the first fracture event with this specimen, the crack on each side of the hole jumped to a length (average of top and bottom lengths) of 1.6mm from the crowns of the hole. As the load was increased the crack grew to 2.0mm and then 2.3mm. The load was removed and the specimen was placed directly in a pre-heated vise within the oven set to 85°C. Pressure was applied normal to the crack plane to a level of about 0.35 MPa. The specimen remained at this temperature for 10 hours. The clamping pressure was then removed and the temperature was elevated to 95°C and held for a duration of 3 hours, after which the specimen was slowly cooled to room temperature.

The dimensions of the specimen were measured to ensure that no change in shape had occurred due to the thermal treatment. The specimen was then visually inspected under 4x magnification. A light was positioned behind the specimen to reflect off the fracture plane. Typically the healed specimen would bear minor evidence of the previous crack plane in the form of scar-like striations. It was further noted that the initial pre-cracks created by the blade were clearly evident after the healing process. The light reflecting from the pre-cracks was significantly more intense than the light reflecting off the healed interface, indicating that the material on either side of the pre-cracks was still distinctly separated. A typical picture sequence
for the fracture and healing process is given in Figure 7-4. After making these observations the specimen was then loaded in an identical manner that was used for fracturing of the specimen in its virgin state.

During re-loading of the healed specimen, it was noted that the crack grew in a more stable manner compared to crack propagation in the virgin case. As a result the crack grew in smaller increments and at lower velocity, thus yielding a greater number of data points per unit crack length. This was likely due to the fact that the material had previously cracked along the same plane. The fracture proceeded with a similar load vs. crack length data to the virgin fracture to suggest nearly complete healing.

The specimen was fractured, healed and re-fractured for five consecutive cycles, using the above-outlined procedure. During the 2\textsuperscript{nd} and 3\textsuperscript{rd} fracturing cycles (following the 1\textsuperscript{st} and 2\textsuperscript{nd} healing cycles, respectively), the load was removed when the crack had propagated to approximately the same length as that obtained in the virgin state. On the 4\textsuperscript{th} fracturing cycle, the crack was propagated beyond the original length and into previously uncracked material. As such, this extension of the crack can be considered occurring within virgin material. In fracture cycle 5 (after healing cycle 4) the crack was extended to approximately the same length as in fracture cycle 4. On fracture cycle 6, the loading was continued until the crack had propagated to within a few millimeters of the ends of the specimen, which may have introduced inelastic deformation of the specimen at its ends and at the horizontal crowns of the hole. The same healing treatment was performed and it was noted that the crack had disappeared
over just a portion of the entire interface, further suggesting the effect of the permanent deformations mentioned above. Due to this, during fracture cycle 7, very little load was required to propagate the partially healed crack back to its full length, indicating that minimal healing had actually occurred. Thus, because of the inelastic deformation during the preceding severe fracturing, the cracked surfaces did not come back into complete contact under the pressure that was applied. Also, since the crack had grown to the far ends of the specimen, it was likely that the crack faces did not match up again since there is more surface topology to "key" back together. The results of these fracture-healing cycles are presented in Figure 7-5 and Figure 7-6, as applied axial compressive stress vs. crack length, excluding the results obtained for the damaged specimen in the last cycle. The length refers to the average of the top and bottom crack lengths, \( l \), normalized with respect to the radius of the central hole, \( R \). Each set of data points is identified by its state prior to each fracturing process; e.g., "Healing 2" refers to fracturing data after the specimen had been healed for the second time.
Table 7-2 lists the healing efficiencies for specimen 1 and indicates how close the crack length in the healed and virgin cases was in terms of a positive (longer than the virgin crack) or negative (shorter than the virgin crack) percentage. The average healing efficiency, $\eta_{avg}$, for each cycle is listed in the right-most column.

Figure 7-5. Stress vs. crack length data of 5 fracture-healing cycles for specimen 1. All healing treatments for specimen 1 consisted of applying pressure while heating to 85°C for 10 hours followed by heating to 95°C for 3 hours with no applied pressure.
Figure 7-6. Initial portion of stress vs. crack length data shown in Figure 7-5 for specimen 1.
Table 7-2. Healing efficiency of Specimen 1.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_{\text{crit}}$ (MPa)</th>
<th>Healing efficiency $\eta$</th>
<th>$\frac{l-l_{\text{avg}}}{l_{\text{avg}}}$</th>
<th>$\sigma_{\text{crit}}$ (MPa)</th>
<th>Healing efficiency $\eta$</th>
<th>$\frac{l-l_{\text{avg}}}{l_{\text{avg}}}$</th>
<th>$\sigma_{\text{crit}}$ (MPa)</th>
<th>Healing efficiency $\eta$</th>
<th>$\frac{l-l_{\text{avg}}}{l_{\text{avg}}}$</th>
<th>$\eta_{\text{avg}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin fracture</td>
<td>27.7</td>
<td>--</td>
<td>--</td>
<td>29.4</td>
<td>100%</td>
<td>2.3%</td>
<td>31.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Healing 1</td>
<td>25.9</td>
<td>93%</td>
<td>-7.3%</td>
<td>29.4</td>
<td>100%</td>
<td>2.3%</td>
<td>30.8</td>
<td>100%</td>
<td>-4.6%</td>
<td>98%</td>
</tr>
<tr>
<td>Healing 2</td>
<td>26.1</td>
<td>94%</td>
<td>-5.2%</td>
<td>29.4</td>
<td>100%</td>
<td>2.3%</td>
<td>30.8</td>
<td>100%</td>
<td>-4.6%</td>
<td>98%</td>
</tr>
<tr>
<td>Healing 3</td>
<td>28.6</td>
<td>103%</td>
<td>-1.2%</td>
<td>30.3</td>
<td>103%</td>
<td>-1.0%</td>
<td>32.0</td>
<td>103%</td>
<td>-0.2%</td>
<td>103%</td>
</tr>
<tr>
<td>Healing 4</td>
<td>29.2</td>
<td>106%</td>
<td>5.9%</td>
<td>31.7</td>
<td>108%</td>
<td>2.4%</td>
<td>32.5</td>
<td>105%</td>
<td>-6.0%</td>
<td>106%</td>
</tr>
<tr>
<td>Healing 5</td>
<td>27.9</td>
<td>101%</td>
<td>-6.9%</td>
<td>31.3</td>
<td>106%</td>
<td>-0.1%</td>
<td>32.9</td>
<td>106%</td>
<td>-2.4%</td>
<td>104%</td>
</tr>
</tbody>
</table>

**Specimen 2**

Specimen 1 demonstrated the ability of the 2MEP4F polymer to heal at various lengths along the crack path, over 5 cycles of cracking and healing. In specimen 2, similar measurements were performed, but the duration of the heat treatment was reduced. It was observed in specimen 1 that the crack would essentially disappear when the specimen had reached thermal equilibrium in the oven at about 85°C, which would occur within about 5 minutes; further discussion on this observation is detailed below. The specimen was kept at this temperature for 10 hours (overnight) both as a precaution and for experimental convenience. For specimen 2, the first healing treatment followed the same routine as for specimen 1 to substantiate those results, where the specimen was held at 85°C for 10 hours under pressure, followed by 3 hours at 95°C without pressure. For healing treatments 2 and 3 the thermal treatment time
was reduced to holding at 85°C for 1 hour with pressure, followed by 1 hour at 95°C without pressure. Reducing the treatment time by this amount seemed to have no effect on the healing efficiency of specimen 2. For healing treatment 4, the thermal treatment time was further reduced to holding at 85°C for 30 minutes with pressure, followed by 30 minutes at 95°C without pressure. Again this treatment showed little effect on the healing efficiency of specimen 2. In healing treatment 5, specimen 2 was held at 85°C for 30 minutes with pressure and visually the degree of repair was similar to previous treatments at the same time and temperature. The additional treatment at 95°C was not carried out in treatment 5. The crack initiated at a relatively low load and then extended to a length comparable to the crack in the previous fracture cycle, indicating very low healing efficiency. Upon further loading the crack extended to near the full length of the specimen at a stress well below what was expected by the previous trends. This test indicated the importance of the secondary treatment at 95°C. All results for this specimen are given in Figure 7-7, Figure 7-8 and Table 7-3.
Figure 7-7. Effect of different healing treatments on the resulting fracture strength of specimen 2.
Figure 7-8. Initial portion of stress vs. crack length data shown in Figure 7-7 for specimen 2.
Table 7-3. Efficiency of different healing procedures for specimen 2.

<table>
<thead>
<tr>
<th></th>
<th>Crack length $l/R = 1.04$</th>
<th>Crack length $l/R = 1.15$</th>
<th>Crack length $l/R = 1.30$</th>
<th>$\eta_{\text{avg}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin fracture</td>
<td>$\sigma_{\text{crit}}$ (MPa)</td>
<td>$l/l_{\text{virgin}}$</td>
<td>$\sigma_{\text{crit}}$ (MPa)</td>
<td>$l/l_{\text{virgin}}$</td>
</tr>
<tr>
<td></td>
<td>$\eta$</td>
<td>--</td>
<td>$\eta$</td>
<td>--</td>
</tr>
<tr>
<td>Healing 1</td>
<td>29.0</td>
<td>--</td>
<td>--</td>
<td>29.2</td>
</tr>
<tr>
<td>Healing 2</td>
<td>28.4</td>
<td>98%</td>
<td>-6.5%</td>
<td>30.4</td>
</tr>
<tr>
<td>Healing 3</td>
<td>28.6</td>
<td>99%</td>
<td>-1.1%</td>
<td>29.5</td>
</tr>
<tr>
<td>Healing 4</td>
<td>27.4</td>
<td>95%</td>
<td>-15.9%</td>
<td>29.2</td>
</tr>
</tbody>
</table>

**Specimen 3**

Specimen 3 was used to substantiate the results obtained from specimen 2, namely continuing the healing treatment at 85°C for 30 minutes under pressure, followed by 95°C for 30 minutes without pressure. Again, this healing treatment showed near complete repair over four fracture-healing cycles. During the 4th loading, the crack was extended to near the full length of the specimen. The specimen was healed and re-fractured, showing essentially complete recovery of the previous fracture characteristics over the entire crack length. Figure 7-9, Figure 7-10 and Table 7-4 summarize the results for specimen 3.
Figure 7-9. Fracture and healing on specimen 3.
Figure 7-10. Initial portion of stress vs. crack length data shown in Figure 7-9 for specimen 3.
Table 7-4. Healing efficiency of specimen 3.

| Specimen 4 | To estimate the fracture toughness of the virgin material, a single specimen was subjected to complete fracture to establish the characteristic stress vs. normalized crack length. No healing was carried out on this specimen. The results were then used in conjunction with the model that had already been developed for long and short cracks in a DCDC sample; see Plaisted et al. (2006). The final results of this model are outlined below and compared with the data of specimen 4. |

7.5 Correlation to the Model

To model the crack growth phenomenon in a DCDC sample, Plaisted, et al. (2006) consider first a pair of short cracks emanating from the crowns of the central hole and growing axially under a monotonically increasing axial compression, and seek to estimate the resulting stress-intensity factor. To this end, they represent the
tensile stress field, created by an axial, uniform compression in an infinite plate normal to the axial plane that passes through the center of the hole, by an equivalent pair of concentrated forces of magnitude $P$, acting at the distance $x$ from the center of hole, where

$$P = R d \sigma_0(l),$$  \hspace{1cm} \text{Equation 7-2}$$

$$x = e R.$$  \hspace{1cm} \text{Equation 7-3}$$

Here, $\sigma_0(l)$ is the axial compression, $l$ is the crack length, and $d = 1/\sqrt{27}$ and $e = 3\sqrt{3}(2 - \ln 3)/4$ for an infinite plate. The resulting stress intensity factor can now be readily calculated, leading to the following expression:

$$\frac{\sigma_0(l) \sqrt{w}}{K_c} = \frac{\sqrt{w/R} \sqrt{\pi (1 + \lambda)}}{d \left( \sqrt{1 + \lambda + e} + \sqrt{1 + \lambda - e} \right)},$$  \hspace{1cm} \text{Equation 7-4}$$

where $w$, the half-width of the sample, and $K_c$, the critical stress intensity factor, are used to make the equation dimensionless, and $\lambda = l/R$. To account for the fact that the sample width, $w$, is finite, we now let $d$ be a function of $l/R$ and based on data reported by Plaisted, et al. (2006), set

$$\frac{d(w/R)}{d_w} = 5.7 - 0.75 \frac{w}{R},$$  \hspace{1cm} \text{Equation 7-5}$$

where $d_w = 1/\sqrt{27}$. Note that the linear approximation (Equation 7-4) has a limited range of applicability, but should be sufficient for our current geometry. Equation 7-3, with approximation (Equation 7-4), is valid while the crack is relatively short. For the
long-crack approximation, we consider a beam-column model, and as detailed in Plaisted, et al. (2006), arrive at the following expression for the axial stress vs. crack length:

$$\frac{\sigma_x \sqrt{w}}{K_e} = \frac{w/R}{2g(w/R)}.$$  \hspace{1cm} \text{Equation 7-6}

where the function $g(w/R)$ is given by

$$g(w/R) = \frac{3 + 2\ln(w/R)}{4(w/R)} - \frac{1}{4(w/R)^2}.$$  \hspace{1cm} \text{Equation 7-7}

Equation 7-5 suggests that the axial stress remains constant once the crack is suitably long. A more complete estimate shows that the axial stress should increase slightly as the crack length increases.

To estimate the $K_e$ of the material, we use Equation 7-5 and Equation 7-6, together with the plateau value of the axial stress. We then use this value of $K_e$ in Equation 7-3 to model the short crack growth regime. From Figure 7-11, the plateau value of the axial stress is about 43 MPa, which yields a value of about 0.69 MPa$\cdot$m$^{1/2}$ for the fracture toughness. With this value, the solid curves in Figure 7-11 are obtained. As an additional comparison, we have also included in this figure the results obtained after the fifth cycle of fracturing and healing for specimen 1, which suggest some increase in the fracture toughness due to repeated healing. In this case, the plateau value is 44.3 MPa with a fracture toughness of 0.72 MPa$\cdot$m$^{1/2}$.
Figure 7-11. Fracture into virgin polymer for specimen 4 in relation to model prediction with $K_c = 0.692 \text{ MPa}\cdot \text{m}^{1/2}$, and specimen 4 after 5 cycles of fracturing and healing with $K_c = 0.716 \text{ MPa}\cdot \text{m}^{1/2}$.

### 7.6 Discussion

These experiments have demonstrated the healing efficiency of the 2MEP4F polymer to be near complete over several cycles of fracturing and healing, using a healing process at moderate temperatures and pressures so that no dimensional changes are introduced due to creep. The DCDC sample geometry has demonstrated its utility in allowing quantitative evaluation of the fracture toughness of the virgin and healed polymer. The effect of different healing treatments on the fracture strength of the healed polymer, using various healing periods and temperatures, has been explored. The results clearly demonstrate the repeated healability of this class of polymers. They are in contrast to the previous fracture-healing studies of this class of polymers that have used high temperatures at which the polymer loses its stiffness and
in fact can be molded into different geometries (Chen et al. 2002; Chen et al. 2003). Notwithstanding the high temperature treatments, Chen et al. (2003) obtain for 2MEP4F polymer a healing efficiency of 78% for a treatment at 115°C and an efficiency of 41% at 120°C, and 50% at 150°C for 3M4F polymer, at which temperatures both polymers would undergo extensive creep under small pressures. Indeed, healing at these temperatures results from the repair both the fractured bonds and the thermally liberated bonds (bonds broken due to the retro-DA reaction at those elevated temperatures), whereas at temperatures used in the present experiments, healing only occurs between fractured bonds. Multiple healing events are shown to be possible along the same fracture path and are most repeatable when the crack length is kept below the plateau value of the axial stress as described in our model, to avoid excessive bending that would produce inelastic deformation in the sample.

Optical observations indicated that healing in 2MEP4F was noted to occur within 10 minutes at 85°C, though it may be incomplete. Further heating to 95°C, a temperature around the onset of the glass transition, provides additional energy for the remaining unreacted moieties to re-combine. At this temperature, the applied pressure is removed to avoid creep within the specimen since the stiffness of the material is reduced. In theory, the bond will self-repair at temperatures below 110°C provided that the broken moieties come into contact. Heating provides sufficient conformational motion in the polymer structure to bring the de-bonded maleimide and furan groups into close proximity. Chen et al. have shown that polymerization
between similar furan and maleimide moieties at room temperature requires many
days and reaches only 60-70% cross-linking (Chen et al. 2002; Chen 2003).

The data suggests that the degree of healing does not increase with increasing
the treatment time beyond 1 hour. Similar healing efficiencies were obtained for the
10 hour (85°C) followed by 3 hour (95°C) treatment as for the 0.5 hour (85°C)
followed by 0.5 hour (95°C) treatment. Figure 7-12 illustrates in-situ photos of
progressive stages of healing during the thermal treatment of specimen 3. These
photos provide an estimate of when the crack undergoes most of its (visual) repair.
At about 4 minutes after being placed in the oven at 85°C, the crack essentially
disappears. Calculations, based on the heat capacity 1.3 J/g°C and an estimated
thermal conductivity (0.25 W/m°C average for polyimides), indicate that it should
take about 3 minutes for the center of the sample to reach 85°C. During initial
polymerization of these monomers at 95°C, the mixture begins to gel within about 3
minutes after combination. Likewise the re-polymerization of bonds across the
cracked interface is also rapid at these temperatures.
Figure 7-12. Illustration of in-situ photos of representative healing treatment at 85°C. Top – orientation of sample with respect to camera. Crack is indicated by dotted line. Bottom – Sequence of photos during treatment at 85°C. (A) Time 0. (B) 2 minutes (C) 4 minutes (D) 15 minutes.

That the degree of healing does not improve with time beyond that required to reach thermal equilibrium is in contrast to the healing observed in the welding of thermoplastics polymers (Wool and O'Connor 1982; Kausch and Tirrell 1989; Wool 1995). The recovery of strength in welded thermoplastic shows a time dependence
that corresponds to the diffusion of polymer chains across the interface. Healing in the 2MEP4F polymer occurs rapidly at 85°C, after the sample has reached thermal equilibrium, which indicates it is not a diffusion-controlled process; rather it occurs on a time scale controlled by the kinetics of the Diels-Alder reaction to re-connect the broken cross-linking bonds that then leads to the recovery of the overall macroscopic fracture toughness.

The data suggests that the samples became slightly more resistant to fracture with successive healing treatments, a trend that was observed consistently for all three samples. One may suspect that the increased thermal treatment renders the sample stronger perhaps due to an increase in the degree of conversion in the polymerization. This however is not supported by the fact that shorter thermal treatments resulted in the same full recovery as the longer treatments. Also, samples were cured for 15 hours at 100°C to maximize the degree of conversion during polymerization. Thermal analysis by differential scanning calorimetry had indicated no further change in the polymer after this treatment.

Another possible cause may be due to the difference in velocity of crack propagation in the virgin and healed cases. In the virgin material, the sample would incrementally build up elastic energy with increasing applied load, and upon reaching a critical stress the crack would rapidly propagate some distance before arresting. Then this process would be repeated for the next incremental crack growth. Fracture through the healed interface proceeded in a more gradual manner, as indicated by the
greater number of data points per length of crack propagation in the healed samples. There was less buildup of elastic energy before the crack would propagate. As such the crack would propagate at a lower velocity and could be arrested after traveling a smaller distance, which would appear in the data as bearing a greater stress for a given crack length. This suggestion would imply imperfect healing along the crack plane, though in the data it would give the appearance that the sample had healed to a greater degree than the original material.

### 7.7 Acknowledgement

This results presented in the previous sections of this chapter are to appear in “Quantitative Evaluation of Fracture, Healing and Re-healing of a Reversibly Cross-linked Polymer”, *Acta Materialia*, 2007, Plaisted T.; and Nemat-Nasser S., published by Elsevier. The dissertation author was the principle investigator and author on this research.

### 7.8 Appendix: Fracture and Healing with $w/R$ Ratio 3

This section describes fracture and healing experiments performed on specimens of 2MEP4F in the DCDC geometry with a $w/R$ ratio of approximately 3 (actual value 2.76). Difficulty in controlling the extent of the crack propagation with this sample justifies the use of DCDC specimen with $w/R$ ratio of 4, as was used in the experiments described in the previous sections of this chapter. However, if the length of the crack can be kept below the plateau regime, near full recovery of fracture toughness is again observed. Healing experiments on the two specimen reported here
demonstrate that extending the crack close to or beyond the plateau stress will introduce inelastic deformation in the specimen in the regions around the hole for specimen with \( w/R \) ratio 3. The degree of plastic deformation is not sufficiently large that it can be noticed by the naked eye; the specimen essentially returns to its original geometry when the axial compression is removed. The last photo in the sequence of Figure 6-5 qualitatively illustrates the degree of outward deflection when the crack grows into the plateau regime of a PMMA sample. The last photo in Figure 6-6 shows how the specimen returns to the original geometry when the axial compression is removed, and the remaining stresses in the regions around the hole after the fracture event.

In terms of healing experiments, plastic deformation within the specimen affects the stress required to reopen the crack during the re-fracture of a healed specimen. When the crack faces are brought back into contact through applied pressure, the plastic deformation remains in those regions and imparts a force to return the specimen to its plastically deformed shape, thus reducing the force required to re-open the crack.

The reduced healing efficiencies derived from fracture tests on specimen 5 (with \( w/R \) ratio 3) are illustrated in Figure 7-13. In these tests, the samples were pre-cracked with the confining fixture, to a length that was already very close to the plateau limit. For the \( w/R \) 3 geometry for the 2MEP4F polymer, the limit occurs when the crack reaches a length (relative to the radius of the hole) \( l/R \) of about 1.4. The
model for this geometry and 2MEP4F with a fracture toughness of 0.69 MPa·m^{0.5} is given in Figure 7-13 by the solid lines. The pre-crack was introduced to a length approximately $l/R$ of 1. Upon removal of the clamp and application of axial compression, the crack jumped to a length of about $l/R$ of 4. At this length plastic deformation was likely introduced. Upon healing, the crack somewhat disappeared, but the stress required to extend the crack back to that length was significantly lower that the stress in the virgin material. Three additional fracture and healing treatments showed progressively lower healing efficiencies.

![Graph showing fracture and healing of specimen 5 with $w/R$ ratio of 3. Poor healing efficiency observed when the virgin crack length is extended into the plateau regime.](image)

Figure 7-13. Fracture and healing of specimen 5 with $w/R$ ratio of 3. Poor healing efficiency observed when the virgin crack length is extended into the plateau regime.

An additional sample, specimen 6, was fabricated with the same geometry, though the pre-crack length in this specimen was propagated to a length $l/R$ of about
0.5. With the pre-cracking fixture removed and the application of axial compression, the crack was then extended to $l/R$ of 1.3, which is slightly below the plateau limit. Subsequent healing and re-fracturing showed near complete healing for four cycles. These results are shown in Figure 7-14. There is little control over the length to which the crack extends without the lateral confining fixture when the polymer specimen are fabricated with a $w/R$ ratio of 3. That the crack stopped at a length below the plateau limit was somewhat fortunate in the case of this specimen. Hence it was decided to make all future specimens with a $w/R$ ratio of 4, which provides a much greater window over which the crack grows in a stable manner.

![Graph showing fracture cycle](image)

Figure 7-14. Specimen 6 with $w/R$ ratio of 3. Near complete healing efficiency is observed when virgin crack length is kept below the plateau region.
Figure 7-15. Fracture and healing sequence of a specimen 6. A) Virgin sample with hole and pre-cracks visible; B) Sample after first fracture event with identical cracks extending from top and bottom of hole; C) Sample after first healing treatment; D) Sample after second fracture event.
8 Microcrack Healing in Polymer Composites

Glass and carbon fiber-reinforced composites have been fabricated with 2MEP4F healable polymer as the matrix material. In the present work, the ability of this thermally-reversible cross-linked polymer to heal microcracks in fiber-reinforced composites is demonstrated. Microcracks have been introduced into the composites by cryogenic cycling in liquid nitrogen. The microcracks reduced the modulus of the composites by up to 10% for the carbon sample and 3% for the glass sample, as measured using a Dynamic Mechanical Thermal Analyzer (DMTA). This reduction in the storage modulus was due to transverse microcracks within the plies of [90/0]s laminates. Heating the laminate, with pressure applied normal to transverse microcracks, appeared to repair the cracks and partially recover the composite's stiffness. The repair of microcracks was also confirmed through optical micrographs. The healing efficiencies of the two glass composite samples, averaged over the 5 frequencies tested, were 99.8% and 98.4%, following a reduction in storage modulus to 96.7% and 96.9%, respectively. The healing efficiencies of the two carbon composite samples were 95.7% and 95.9%, following a reduction in storage modulus to 90.6% and 89.8%, respectively. Not all microcracks were repaired in every specimen, suggesting that perhaps additional pressure could improve the healing scenario and that a complete healing of the neat polymer does not necessarily guarantee a full healing of the corresponding composites without some optimization of the healing process. A DMTA scan of the carbon composite illustrated that softening of the sample did not occur until about 110°C and the glass transition measured by the
peak of the tan delta was in the range of 119°C. These temperatures are well above the thermal treatment temperature used in this study to induce repair.

8.1 Introduction

Highly cross-linked polymer matrices, commonly used in fiber-reinforced composites, are notorious for their propensity to form microcracks. The cracks are often among the first forms of mechanical damage in fiber-reinforced polymer composites (Owen and Dukes 1967; Owen and Howe 1972; Talreja 1981; Wang et al. 1983; Wang et al. 1986; Talreja 1989; Nairn and Hu 1994), typically propagating along the direction parallel to the fibers in each ply of the laminate. Microcracks may be formed during manufacturing due to mismatch in the coefficient of thermal expansion (CTE) of the fiber and matrix if the material is improperly cured. Thermal or mechanical cycling, particularly in fatigue loading applications, may also create microcracks. These cracks exist on a length scale of a few micrometers and though they may not immediately compromise the integrity of the material in certain situations, they can lead to ultimate failure in others. Further loading, particularly in fatigue, may cause these cracks to propagate into macrocracks and delaminations that can eventually cause the composite to fail. Moreover, microcracks provide an entrance point for corrosive contaminants to further degrade the material. In storage applications, these cracks allow material to leak from the container. A polymer matrix with the ability to repair these cracks before additional damage can occur is therefore of considerable interest.
Healing damage within a polymer is most often associated with the softening and flow of material across a damaged interface that occurs upon heating a thermoplastic polymer. This technique is commonly known as thermoplastic welding. Healing in thermoplastic polymers occurs largely due to the restoration of entanglements in the polymer interface. Chains are able to diffuse across the interface when heated above the glass transition temperature, $T_g$. The rate of crack healing is strongly time-dependant, as the once separated molecular structures diffuse across the interface to form a bonding state equivalent to that of the virgin material. Crack healing in thermoplastic polymer surfaces seldom results from the re-formation of broken primary bonds in the polymer backbone. Typically, the polymer chains at the crack interface have been irreversibly damaged through bond breakage, which results in an average molecular weight significantly lower than that of the bulk polymer.

Healing damage by thermal treatments in thermoset polymers is not possible due to the cross-linked nature of these materials. The cross-link network prevents the polymer chains from diffusing through the material when heated above the $T_g$. Rather the material begins to thermally degrade when heated excessively and, in contrast to thermoplastics, cannot be returned to its original state. Until recently, there has been no evidence of repairing damage in highly cross-linked materials. An interesting repair scheme has been proposed by White et al., where a healing system is embedded within an epoxy polymer (White et al. 2001).
In current high-performance composite applications, thermoplastics are not widely used due to inferior mechanical and processing characteristics compared to thermoset polymers such as epoxies and vinyl esters. Although they tend to be tougher and more ductile, they are typically more prone to fatigue degradation and accumulate microcracks and debond more rapidly than thermosets (Gamstedt and Talreja 1999). Furthermore, the processing techniques to obtain a defect-free composite are not well established due to the high melt viscosity of most thermoplastics that complicates impregnation of the polymer into a fiber preform. The thermoplastics that do possess good mechanical properties, such as polyetheretherketone (PEEK), also exhibit a semi-crystalline structure. Crystallinity impedes the diffusion of broken polymer chains across a damaged interface at temperatures around the glass transition temperature. Rather, the polymer must be heated close to or above its melting temperature to achieve healing (Davies et al. 1989). In many applications, heating a material to such high temperatures, and moreover to a degree that causes the material to liquefy, is impractical.

8.2 Thermally-reversible Cross-linked 2MEP4F Polymer

Researchers at the Exotic Materials Institute at UCLA developed a polymer with the ability to repair internal cracking based on a thermally-reversible Diels-Alder (DA) and retro-DA cycloaddition (Chen et al. 2002; Chen et al. 2003). The repair mechanism of these polymers relies on the reversibility of the Diels-Alder (DA) bonds. Figure 8-1 shows the reaction and DA adduct for one such formulation that incorporates two maleimide moieties for every four furan moieties, which is referred
to hereafter as 2MEP4F polymer. This DA covalent bond is weaker than other bonds in the backbone polymer, so that, when the sample is loaded excessively, it will break preferentially there as compared to the other covalent bonds in the molecule. Above \(\sim110^\circ C\), the bonds will also disconnect by retro-DA cycloaddition. Below 110\(^\circ\)C, the stable state of the DA moieties is to re-connect as a cycloadduct. Thus, healing is achieved by bringing the broken DA moieties into proximity of one another at a temperature below 110\(^\circ\)C. This suggests that macrocracks in the polymer can be healed by bringing the fractured interfaces together through pressure at suitable temperatures to accelerate healing while avoiding creep, and then allowing them to re-connect by cooling the polymer to room temperature. Heating provides sufficient conformational motion in the polymer structure to bring the de-bonded maleimide and furan groups into close proximity. In theory, the bond will self-repair at any temperature below 110\(^\circ\)C, provided that the broken moieties come into contact.

![Diagram of 2MEP4F polymer](image)

Figure 8-1. The polymer consists of a multifuran molecule combined in stoichiometric ratio with a multimaleimide molecule to form 2MEP4F cycloadduct.
8.3 Polymer Processing into Fiber Composite

Bismaleimide (2MEP) and tetrafurane (4F) monomers were prepared according to procedures outlined in the literature (Chen, et al. 2002, Chen, et al. 2003). At room temperature, 2MEP is a solid and 4F is a liquid with viscosity in the range of 1500 cP. Mixing and infusion into a fiber preform is improved by combining the two components in the liquid state at a temperature above the melting temperature of 2MEP (84°C), though gelation of the prepolymer proceeds more rapidly at such temperatures. A molding apparatus was developed for rapid injection of the liquid monomers at elevated temperature and under vacuum into a fiber preform (Figure 8-2). Polymerization was carried out in the following way. Monomer 2MEP was heated above its melting point to a temperature of 95°C. Furan monomer 4F was likewise heated to 95°C to reduce its viscosity (below 100 cP) and the two monomers were combined in stoichiometric proportion and mixed under vacuum for about thirty seconds. The injection molding apparatus was pre-heated to 95°C within a hot press and the lower portion of the injection apparatus containing the fiber preform was evacuated to a level less than 1 Torr. The prepolymer was poured into the injection apparatus and pressure was applied to the injection cylinder to perforate a thin polytetrafluoroethylene membrane dividing the two chambers, allowing the prepolymer to infuse into the fiber preform. At this temperature the polymer would gel within about 3 minutes and a hard polymer would result within about 30 minutes. To ensure complete polymerization the samples were held at 100°C for fifteen hours after injection. The polymerized samples were then cooled to room temperature over a period of ten hours and demolded from the injection apparatus.
Two types of fiber reinforcements were infused with 2MEP4F polymer using the above procedure. Toray T300 carbon fiber, supplied as unidirectional fabric consisting of tows (3K) held in position with fine fill fibers, was infused using the above method. Likewise S-2 glass fiber (from AGY) in the same unidirectional form was also processed in a separate infusion. Layers of unidirectional fiber were stacked in [90, 0, 0, 90] orientation within the infusion apparatus.
8.4 Test Method

The goal of this study was to measure the efficiency of microcrack healing in 2MEP4F polymer composites. The experiment required a method to introduce quantifiable microcracks into the matrix of fiber-reinforced 2MEP4F polymer that could then be subjected to a thermal treatment to repair those cracks and measure the degree of the resulting recovery. Microcracks typically form in the intralaminar regions of a composite parallel to the direction of the fibers, referred to as transverse matrix cracks. They can extend through the entire length and width of a lamina, though they are typically arrested in the out-of-plane direction at the border with the adjacent lamina that possesses a different fiber orientation. For this study a symmetric and balanced layup sequence of [90/0], was selected that would allow the laminate to remain intact after microcracking due to the two fiber orientations. The orientation of the laminate within the measuring device was also important to allow detection and quantification of the degree of microcracking and healing. Lincoln et al. employed this specimen layup to study the formation of transverse microcracks in carbon/bismaleimide composites, using dynamic mechanical analysis in bending (Lincoln et al. 2001). The laminate is orientated within a single cantilever bending grip such that the microcracks in the outermost plies are transverse to the maximum tensile and compressive forces on the specimen, thus improving detection and quantification of these cracks (Figure 8-3).

Microcracks were introduced into the laminate by thermal cycling. Due to the mismatch in coefficient of thermal expansion of the fiber and polymer phases,
intralaminar tensile forces led to microcracks transverse to the beam, as the polymer contracted upon cooling (Figure 8-3). In a separate case, a sample was thermally cycled and then fatigued at low temperature to introduce microcracking. The change in bending stiffness in the cantilever beam was measured before and after the microcracking treatment. The samples were heated within an oven and with a compression fixture to initiate a healing mechanism. The samples were then cooled to room temperature and the bending modulus re-measured.

Figure 8-3. Single cantilever beam of [90/0]_s laminate tested using Dynamic Mechanical Thermal Analysis to quantify microcracking and subsequent healing of healable composite.

8.5 Sample Preparation

Composite samples were fabricated in the injection apparatus to 76mm x 76mm x 1mm panels. Due to the rapid injection process, fibers were displaced from the central region of the panel directly beneath the injection point. After curing and demolding, 7mm x 35mm x 1mm beam specimens were cut with a diamond blade from sections of the panel, avoiding the fiber depleted regions. The edges of these samples were polished with 0.3μm alumina slurry and photographed. Volume fraction calculations based on representative micrographs put the fiber volume fraction around 60-65%.
After polishing, samples were dried in a dessicator for 2 days. Samples were then inspected under a microscope for processing flaws. There were a few defects, mainly consisting of voids or resin depleted regions on or near the surface of the sample. The samples were then mounted in a TA Instruments 2910 Dynamic Mechanical Thermal Analyzer within a single cantilever bending fixture and tightened within the clamps to a uniform and repeatable torque of 0.9 Nm. The alignment and orientation of each specimen was carefully noted for identical placement in subsequent measurements.

8.6 Measurement

The storage modulus and loss tangent of the cantilever beam were measured in multifrequency mode. In the multifrequency mode, the sample was oscillated to an amplitude of 50µm at frequencies of 100, 25, 10, 1 and 0.1Hz. To account for the effect of sample placement within the clamps, the sample was then removed from the machine and replaced within the grip and repeated for a total of three measurements which were then averaged.

Microcracking the composite consisted of thermally cycling the composite by submersing it in liquid nitrogen for a period of 5 minutes, then slowly returning it to room temperature. Thermal equilibration was carried out within a dessicator under vacuum to ensure no moisture condensed on the samples. Thermal cycling was carried out between 5 to 20 times to induce significant microcracking as viewed under
an optical microscope. The storage modulus of the samples was then re-measured at room temperature to quantify the reduction in the stiffness due to the microcracks.

8.7 Healing Treatment

Healing treatment consisted of heating the sample within a convective oven to reconnect the debonded furan and maleimide moieties through DA cycloaddition. Pressure was applied normal to the fiber direction of the outermost plies, such that transverse cracks formed in these plies would be brought back together. A dead weight was used to impart pressure through a fixture which held the sample in place. The fixture also consisted of aluminum face sheets to support the sample to prevent out-of-plane buckling as the axial pressure was applied. A schematic of this fixture is given in Figure 8-4. Previous studies of healing macrocracks in neat 2MEP4F polymer had confirmed that time had little effect on the degree of healing of the sample beyond ~30 minutes within the chamber (Plaisted and Nemat-Nasser 2007). For experimental convenience the healing time for each treatment in this study was about 10 hours. Previous studies had utilized a pressure of about 350 kPa to bring the crack interface together for healing neat 2MEP4F polymer. The increased stiffness due to the fiber reinforcement in the composite samples of this study required a greater pressure to close the cracks, though this parameter was not fully explored in this study. Rather a mass of about 1,300 grams was placed on the sample to bear approximately 1.7 MPa in the axial direction of the beam. After thermal treatment the samples were then re-measured at room temperature to quantify the recovery in the storage modulus due to the healing treatment.
Figure 8-4. A. Composite is fabricated in a [90 / 0 / 0 / 90] layup. B. Microcracks are introduced through thermal cycling between room temperature and -196°C. C. Transverse microcracks in the outermost plies are healed through heat and the application of pressure normal to the crack faces in those plies. Single cantilever beam (B) measurement of storage modulus is used to characterize virgin/cracked/healed states of the composite.

### 8.8 Glass Fiber Composites Results

Three glass fiber composites were tested for recovery of modulus after cracking and healing treatments. Glass composite sample 1 was cycled a total of 5 times in liquid nitrogen to introduce microcracks. The storage modulus was reduced to approximately 97% of the virgin value. After heating the sample to 95°C the sample returned to nearly 100% of the original modulus; see Figure 8-5 and Table 8-1.
Glass composite sample 2 was cycled a total of 20 times in liquid nitrogen. The storage modulus after this treatment again decreased to about 97% of the virgin storage modulus. Thermal treatment at 95°C regained about 1.5% of the modulus; see Figure 8-6 and Table 8-2. In both samples it was noted however that not all of the microcracks had healed. Transverse cracks which had formed in the central plies did not heal, as expected, since the direction of applied pressure was parallel to these cracks. Some cracks in the outermost plies, where the applied pressure was acting in a direction to close the crack, also did not fully heal. These cracks were not visible on the opposite side of the specimen which would indicate that the cracks may have healed through a majority of the ply but not completely at the opposite surface.

A third glass fiber composite sample was cycled 20 times in liquid nitrogen. The sample fractured into two pieces upon clamping the sample in the bending grips to re-measure the storage modulus. The resulting fiber fracture and pullout prohibited re-matching the broken halves and healing this macrocrack.
Figure 8-5. Average storage modulus and standard deviation of three measurements for glass composite sample 1 after microcracking and thermal healing treatments.

Table 8-1. Healing efficiency (storage modulus with respect to virgin storage modulus) after cryogenic cycling and thermal healing treatments for glass composite sample 1. Values represent the average of three measurements taken at each of the frequencies.

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>Stiffness Retention (% of virgin storage modulus)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cryogenic Cycling</td>
</tr>
<tr>
<td>100</td>
<td>97.0%</td>
</tr>
<tr>
<td>25</td>
<td>96.7%</td>
</tr>
<tr>
<td>10</td>
<td>96.6%</td>
</tr>
<tr>
<td>1</td>
<td>96.6%</td>
</tr>
<tr>
<td>0.1</td>
<td>96.7%</td>
</tr>
<tr>
<td>AVG</td>
<td>96.7%</td>
</tr>
</tbody>
</table>
Figure 8-6. Average storage modulus and standard deviation of three measurements for glass composite sample 2 after microcracking and thermal healing treatments.

Table 8-2. Healing efficiency after cryogenic cycling and thermal healing treatments for glass composite sample 2. Values represent the average of three measurements taken at each of the frequencies.

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>Stiffness Retention (% of virgin storage modulus)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cryogenic Cycling</td>
</tr>
<tr>
<td>100</td>
<td>97.4%</td>
</tr>
<tr>
<td>25</td>
<td>96.6%</td>
</tr>
<tr>
<td>10</td>
<td>96.8%</td>
</tr>
<tr>
<td>1</td>
<td>96.9%</td>
</tr>
<tr>
<td>0.1</td>
<td>96.9%</td>
</tr>
<tr>
<td>AVG</td>
<td>96.9%</td>
</tr>
</tbody>
</table>
8.9 Carbon Fiber Composites Results

Three carbon fiber composites were tested for recovery of modulus after cracking and healing. Sample 1 was cycled a total of 20 times in liquid nitrogen to introduce microcracks. A gradual reduction of stiffness was noted over intervals of 10, 15 and 20 cycles. After 20 cycles the storage modulus was reduced to 90.6% of the virgin modulus when averaged for the three separate measurements taken at the 5 frequencies investigated. The sample was then heated to 84°C for 10 hours. Treatment at this temperature increased the modulus to 91.4%. The sample was then heated to 95°C under the same pressure and duration which resulted in a further recovery in modulus to 95.7%. Figure 8-8 and Table 8-3 present the data for this sample.

Carbon composite sample 2 was exposed to cryogenic fatigue. The sample was cooled from room temperature at 3°C/minute while being cycled at 1Hz with a displacement of 50µm. Upon reaching -120°C the sample was held isothermal for 30 minutes. Figure 8-7 shows the storage modulus and tan delta as temperature was decreased during this treatment. Abrupt changes in storage modulus and tan delta at -18°C, -53°C, -68°C, -80°C, and -88°C are likely points at which transverse cracks were formed, as has been observed in the literature (Timmerman et al. 2002). The rapid drop in storage modulus at -18°C likely corresponded to the formation of a large crack that was observed close to the grip region. The sample was returned to room temperature over the course of 8 hours and the storage modulus was measured and noted to have decreased to approximately 90% of its virgin storage modulus. Thermal
treatment at 95°C restored the storage modulus to about 96% of the virgin value. Results for this sample are summarized in Figure 8-9 and Table 8-4. It was noted that one large crack remained in the sample (Figure 8-10). Other cracks, such as those photographed in Figure 8-11, were no longer visible after the thermal treatment.

![Graph](image-url)

**Figure 8-7.** Storage modulus and tan delta for carbon composite sample 2 during cooling from 30 to -120°C.

A third carbon fiber sample was exposed to the same cryogenic fatigue cycle as sample 2. A large crack developed across the sample width which, upon removal from the single cantilever bending grips, propagated and caused the sample to fracture into two pieces.

The thermal treatment alone was tested for its effect on the composite storage modulus. The cryogenic cycling step was skipped so that the virgin storage modulus
could be compared to the storage modulus after the thermal treatment at 95°C with applied pressure. There was no increase in storage modulus as a result of the thermal treatment, which verified that the polymer was not becoming stiffer as a result of further heating and curing. This sample was then ramped from 30°C to 135°C at 3°C/minute while measuring the storage modulus in single cantilever bending at 1Hz. The peak in the tan delta indicated a glass transition temperature for the carbon composite of 119°C, shown in Figure 8-12.
Figure 8-8. Average storage modulus and standard deviation of three measurements for carbon composite sample 1 after microcracking and thermal healing treatments.

Table 8-3. Healing efficiency after cryogenic cycling and thermal healing treatments for carbon composite sample 1. Values represent the average of three measurements taken at each of the frequencies.

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>Stiffness Retention (% of virgin storage modulus)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cryogenic cycling</td>
</tr>
<tr>
<td></td>
<td>10 cycles</td>
</tr>
<tr>
<td>100</td>
<td>93.2%</td>
</tr>
<tr>
<td>10</td>
<td>93.4%</td>
</tr>
<tr>
<td>25</td>
<td>93.3%</td>
</tr>
<tr>
<td>1</td>
<td>93.6%</td>
</tr>
<tr>
<td>0.1</td>
<td>93.9%</td>
</tr>
<tr>
<td>AVG</td>
<td>93.5%</td>
</tr>
</tbody>
</table>
Figure 8-9. Average storage modulus and standard deviation of three measurements for carbon composite sample 2 after microcracking and thermal healing treatments.

Table 8-4. Healing efficiency after cryogenic cycling and thermal healing treatments for carbon composite sample 2. Values represent the average of three measurements taken at each of the frequencies.

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>Stiffness Retention (% of virgin storage modulus)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cryogenic Fatigue</td>
</tr>
<tr>
<td>100</td>
<td>89.6%</td>
</tr>
<tr>
<td>25</td>
<td>89.6%</td>
</tr>
<tr>
<td>10</td>
<td>89.8%</td>
</tr>
<tr>
<td>1</td>
<td>89.9%</td>
</tr>
<tr>
<td>0.1</td>
<td>90.1%</td>
</tr>
<tr>
<td>AVG</td>
<td>89.8%</td>
</tr>
</tbody>
</table>
Figure 8-10. Micrographs at 400x of carbon composite sample 2 of crack that did not heal. Crack visible before (top) and after (bottom) healing treatment at 95°C.
Figure 8-11. Micrographs at 400x of carbon composite sample 2 of microcracks that healed. Microcrack visible after cryogenic cycling (top) and healing of those cracks after treatment at 95°C (bottom).
Figure 8-12. Storage modulus and tan delta for carbon composite during heating from 35°C to 135°C.

### 8.10 Discussion

This study demonstrated the ability of a thermally-reversible, cross-linked polymer to heal microcracks in fiber reinforced 2MEP4F polymer composites. The utility of the Dynamic Mechanical Thermal Analyzer to measure small changes in composite modulus due to microcracking and subsequent repair of microcracking was also demonstrated. DMTA measured a reduction in storage modulus due to transverse microcracks within the plies of [90/0]s laminates. Heating the laminate with pressure applied normal to transverse microcracks in the top and bottom plies of the laminate appeared to repair the cracks and was confirmed through optical micrographs. The healing efficiencies, calculated as a ratio of the storage modulus after treatment with
respect to the as-fabricated storage modulus, for the two glass composite samples, averaged over the 5 frequencies tested, were 99.8% and 98.4%, following a reduction in storage modulus to 96.7% and 96.9%, respectively. The healing efficiencies of the two carbon composite samples were 95.7% and 95.9%, following a reduction in storage modulus to 90.6% and 89.8%, respectively.

The storage modulus varied with frequency and was typically higher at 100hz than at 0.1Hz. The storage modulus generally followed the same trend with respect to the frequency in the virgin, cracked, and healed states, but was offset by some amount that reflected the degree of cracking or repair within the sample. Repositioning the sample for each measurement resulted in a small change in the measured storage modulus, where the typical standard deviation was less than a few percent of the average value. Microcracked samples generally showed a greater variation in measured stiffness when the sample was removed and repositioned. This would be expected since the bending modulus is particularly sensitive to the position of the crack along the moment arm in a cantilever beam. An exception to this occurred in carbon composite 2, where the storage modulus after healing treatment at 95°C showed a large variation between the three measurements. The first measurement yielded significantly higher storage modulus values than the following measurements, perhaps an indication that repeated handling/clamping had damaged the specimen.

The degree of microcracking induced by cryogenic cycling up to 20 times in liquid nitrogen appeared to reduce the modulus by about 10% for the carbon sample
and 3% for the glass sample. The difference in degree of cracking may be attributed to the greater mismatch in CTE between the fiber and polymer matrix as well the greater stiffness of the carbon fibers (McManus et al. 1993). Introducing these cracks weakened the samples to a degree that they could break due to further handling/clamping as happened for both a carbon and a glass sample. Additional microcracking would likely be possible with additional cryogenic cycling or perhaps extended fatigue at low temperature, though further precautions would be necessary to avoid complete fracture of the specimen during handling.

Not all microcracks were repaired in every specimen, including glass composite sample 1, which showed near complete recovery of the storage modulus after thermal treatment. This may have been attributed to the cracks having healed through a majority of the ply apart from the interface that was visible from the polished face. In previous tests on the healing of neat 2MEP4F (Plaisted and Nemat-Nasser 2007), a ridge was visible on the surface of samples that had otherwise healed through the thickness of the sample and enabled complete recovery of the original fracture toughness. Perhaps additional pressure could improve the healing scenario to allow full repair of the crack plane in future. A level of applied pressure was selected for these experiments to close the crack faces but this value was not optimized.

It should be noted that heating the sample did not change the shape of the specimen. The temperature used to heal the samples in this study was based on previous healing work on neat 2MEP4F polymer in which macrocracked samples were
heated to 95°C to completely restore the fracture toughness of the material (Plaisted and Nemat-Nasser 2007). A DMTA scan of the carbon composite in the present work illustrated that softening of the sample did not occur until about 110°C and the glass transition measured by the peak of the tan delta was in the range of 119°C. These temperatures are well above the thermal treatment temperature used in this study, which confirms that softening and remolding of the specimen was not responsible for the observed recovery in storage modulus. In contrast to thermoplastic polymers, in which cracks may be repaired by thermal treatment above the $T_g$ to cause material to flow across the interface, the healing in the 2MEP4F polymer is achieved through the repair of broken covalent (Diels-Alder) bonds.
9 Conclusions and Future Research

The results presented in this dissertation have illustrated the incorporation of novel electromagnetic, heating and healing functionalities into polymers and polymer composites. Thin wires and thicker coiled wires have been used to tune the dielectric properties of fiber-reinforced structural composites from negative through positive values. These same wire arrays have been used to resistively heat the composite. The potential for healing and re-healing in polymers containing thermally-reversible cross-links, i.e. the Diels-Alder cycloadduct, has been demonstrated. This healable polymer has also been integrated with continuous fiber reinforcement to create structural composites with the ability to heal microcracks over multiple cycles.

A polymer with a built-in mechanism to repair cracks by restoring broken bonds is of great interest for numerous composite and adhesive applications to extend the service life and improve the safety of structural materials, electronic assemblies, storage tanks, etc. The polymer requires outside intervention to initiate the heating (healing) process. Developments in self-sensing smart materials may offer a solution to this system, where an integrated self-sensing, self-healing composite acts autonomously. Otherwise a periodic maintenance routine would be required to regularly heat the material to return it to its original state. These novel properties may also be applied to healing of cracks within adhesives and bonded joints. The remainder of this chapter briefly touches on a few areas for extended research on this polymer.
9.1 Synergistic Multifunctional Material

One may conceive that the electromagnetic, heating and healing functionalities be combined into a single material. The wires may serve not only as electromagnetic scattering elements, but may further provide channels through which heat is transported to heal cracks within the thermally-reversible polymer. They may be heated resistively if connected to an external current source, or they may act as inductive heaters if external magnetic fields are applied. Since the wires are distributed periodically throughout the composite, heat is also uniformly distributed. There may be further synergy with the fiber reinforcement of the composite such that the reinforcing fibers may also contribute to the healing mechanism. If a fiber with a negative (axial) coefficient of thermal expansion, such as para-aramid (Kevlar®) or PBO (Zylon®), is chosen to reinforce the composite laminate, then it may provide compression to close the crack faces as the material is being heated. Upon heating, a cracked polymer matrix (with a positive CTE as measured for 2MEP4F in 5.3.3) will expand as the reinforcing fibers contract, thus putting the matrix into compression to aid in closing the crack faces.

9.2 Further DCDC and Composite Characterization

Methods for introducing quantifiable cracking and measuring the corresponding healing have been presented in this dissertation. The DCDC geometry has demonstrated great utility in the study of fracture and repair of healable materials due to its ability to arrest a propagating crack before splitting the sample into separate pieces. Moreover it enables multiple fracture events to be measured within a single
testing cycle. Parameters to introduce healing in polymer 2MEP4F have been established though not fully explored. Future work in this area may seek to characterize a wider range of temperatures and pressures required to achieve full and/or partial healing within the neat polymer and composites of this polymer.

Microcracking within the polymer composites was only carried out to reduce the storage modulus by about 10%. Future experiments should seek to understand healing from further degrees of composite microcracking. With more material, larger composite panels may be fabricated and evaluated for recovery of strength and stiffness after other forms of damage, including delamination through testing such as compression-after-impact (Astm 2005).

9.3 Additional Applications of the Reversible DA Bond

The reversible nature of the Diels-Alder bond may be leveraged for other properties than crack healing. As was demonstrated in this work, when heated above the retro-DA temperature, the polymer may be remolded through a reversible polymerization process. The polymer may be heated and remolded much in the same manner as a thermoplastic. Other highly cross-linked polymers, such as epoxies, exhibit only thermosetting characteristics, and as such may not be recycled. The 2MEP4F polymer offers an equivalently strong, stiff polymer that can be reversibly polymerized. Testing of the fracture and healing properties after remolding would provide further useful information on its utility as a recyclable polymer. This characteristic may also make the polymer amenable to processing as a prepreg
material. Composite fabrication by prepreg lamination is a commonly used method to achieve consistent, high fiber volume fraction composites. Individual layers of composite fiber fabric may be impregnated with the polymer, with or without the aid of solvents, and partially or fully cured. The reversible nature of the DA bond may allow layers of this material to be bonded together when later laminated under pressure and heat.

Applied to adhesive joints, the reversible nature of this polymer may enable a bonded joint with the ability to debond with heat (Loy et al. 2000). Adhesive bonding is widely used method to join materials, particularly polymer composites for aerospace applications, where optimizing mechanical and aerodynamic performance and reducing weight and fabrication costs by eliminating mechanical fasteners is achieved. However stress concentrations that exist at the adherend-adhesive interface are often the source of initial failure, in the form of cracks that initiate in the fillet of the adhesive, and eventually propagate toward the bond line and cause catastrophic cohesive and/or adhesive failure (Adams et al. 1997). Inaccessibility often precludes repair, requiring that replacement parts be fabricated. In situations where the bond may be repaired, there is potential for contamination and poor application of repair materials that adversely affect the bond performance (Tomblin et al. 2005). Utilizing a polymer adhesive with the ability to repair cracks before failure would greatly extend the service life of these bonds and eliminate costly repair.
The adhesive properties of the 2MEP4F polymer should be characterized with a variety of adherends, particularly those employed in aerospace applications where this material may be of greatest immediate interest. Lap shear testing, for instance, may be used to characterize the adhesive and subsequent repair properties with aluminum adherends. However, the tendency for the crack to propagate and completely fracture the sample into separate pieces may be undesirable. It may be possible to employ a modified DCDC geometry to study the interface, which has been used in the past to study the fracture resistance of bimaterial interfaces (Turner et al. 1995). Novel testing schemes in which two materials are bonded together with 2MEP4F polymer in the DCDC configuration may enable stable adhesive failure and allow healing studies to be carried out on repaired interfaces.

Figure 9-1. Lap shear joint with typical crack initiation at stress concentration within adhesive fillet zone. These critical locations are where a self-healing polymer will be most effective at repairing damage before catastrophic failure occurs.
Figure 9-2. Expand current DCDC testing to include measurement of fracture resistance of bimaterial interface.
REFERENCES


