

Recent Advances in Smart Self-healing Polymers and Composites

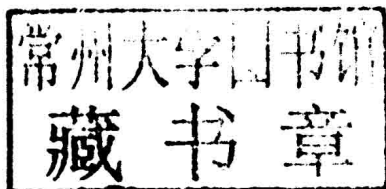
Edited by Guoqiang Li and Harper Meng

Woodhead Publishing Series in Composites
Science and Engineering: Number 58

Recent Advances in Smart Self-healing Polymers and Composites

Edited by

Guoqiang Li and Harper Meng



AMSTERDAM • BOSTON • CAMBRIDGE • HEIDELBERG
LONDON • NEW YORK • OXFORD • PARIS • SAN DIEGO
SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

Woodhead Publishing is an imprint of Elsevier



Woodhead Publishing is an imprint of Elsevier
80 High Street, Sawston, Cambridge, CB22 3HJ, UK
225 Wyman Street, Waltham, MA 02451, USA
Langford Lane, Kidlington, OX5 1GB, UK

Copyright © 2015 Elsevier Ltd. All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means electronic, mechanical, photocopying, recording or otherwise without the prior written permission of the publisher.

Permissions may be sought directly from Elsevier's Science & Technology Rights Department in Oxford, UK: phone (+44) (0) 1865 843830; fax (+44) (0) 1865 853333; email: permissions@elsevier.com. Alternatively you can submit your request online by visiting the Elsevier website at <http://elsevier.com/locate/permissions>, and selecting Obtaining permission to use Elsevier material.

Notice

No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made.

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

Library of Congress Control Number: 2015931792

ISBN 978-1-78242-280-8 (print)

ISBN 978-1-78242-292-1 (online)

For information on all Woodhead Publishing publications
visit our website at <http://store.elsevier.com/>

Printed in the United States of America



**Working together
to grow libraries in
developing countries**

www.elsevier.com • www.bookaid.org

Recent Advances in Smart Self-healing Polymers and Composites

Related titles

Smart Textiles for Medicine and Healthcare
(ISBN 978-1-84569-027-4)

Handbook of Smart Coatings for Materials Protection
(ISBN 978-0-85709-680-7)

Smart Polymers and their Applications
(ISBN 978-0-85709-695-1)

List of contributors

O. Ajisafe Southern University, Baton Rouge, LA, USA

H.P. Cui University of Shanghai for Science and Technology, Shanghai, PR China

W. Deng South China University of Technology, Guangzhou, PR China

Z. Ding Nanyang Technological University, Singapore, Singapore

P. Du Quangang Research Institute of Petrochemical Technology, Fujian Normal University, Petrochemical High-Tech Incubator Base, Quanzhou City, PR China

C.J. Hansen University of Massachusetts Lowell, Lowell, MA, USA

S.A. Hayes The University of Sheffield, Sheffield, UK

W.M. Huang Nanyang Technological University, Singapore, Singapore

A.E. Hughes Deakin University, Geelong, VIC, Australia

G. Ji Louisiana State University, Baton Rouge, LA, USA

M. John Louisiana State University, Baton Rouge, LA, USA

F.R. Jones The University of Sheffield, Sheffield, UK

A.D. Lafferty The University of Sheffield, Sheffield, UK

G. Li Louisiana State University, Baton Rouge, LA, USA; Southern University, Baton Rouge, LA, USA

H. Lu Harbin Institute of Technology, Harbin, PR China

H. Meng Southern University, Baton Rouge, LA, USA

J. Nji Louisiana State University, Baton Rouge, LA, USA

M.Z. Rong Sun Yat-sen University, Guangzhou, PR China

A. Shojaei Halliburton Energy Services, Houston, TX, USA

C.L. Song University of Shanghai for Science and Technology, Shanghai, PR China

T.J. Swait The University of Sheffield, Sheffield, UK

C. Tang Nanyang Technological University, Singapore, Singapore

R.J. Varley CSIRO Manufacturing, Clayton, Victoria, Australia

C.C. Wang Nanjing Institute of Technology, Nanjing, PR China

X. Wang School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai, PR China

J. Wei Nanyang Technological University, Singapore, Singapore

Y. You South China University of Technology, Guangzhou, PR China

A. Zhang South China University of Technology, Guangzhou, PR China

M.Q. Zhang Sun Yat-sen University, Guangzhou, PR China

P. Zhang Louisiana State University, Baton Rouge, LA, USA

Y. Zhao Nanyang Technological University, Singapore, Singapore

D.Y. Zhu Sun Yat-sen University, Guangzhou, PR China; Guangdong University of Technology, Guangzhou, PR China

Woodhead Publishing Series in Composites Science and Engineering

- 1 **Thermoplastic aromatic polymer composites**
F. N. Cogswell
- 2 **Design and manufacture of composite structures**
G. C. Eckold
- 3 **Handbook of polymer composites for engineers**
Edited by L. C. Hollaway
- 4 **Optimisation of composite structures design**
A. Miravete
- 5 **Short-fibre polymer composites**
Edited by S. K. De and J. R. White
- 6 **Flow-induced alignment in composite materials**
Edited by T. D. Papathanasiou and D. C. Guell
- 7 **Thermoset resins for composites**
Compiled by Technolex
- 8 **Microstructural characterisation of fibre-reinforced composites**
Edited by J. Summerscales
- 9 **Composite materials**
F. L. Matthews and R. D. Rawlings
- 10 **3-D textile reinforcements in composite materials**
Edited by A. Miravete
- 11 **Pultrusion for engineers**
Edited by T. Starr
- 12 **Impact behaviour of fibre-reinforced composite materials and structures**
Edited by S. R. Reid and G. Zhou
- 13 **Finite element modelling of composite materials and structures**
F. L. Matthews, G. A. O. Davies, D. Hitchings and C. Soutis
- 14 **Mechanical testing of advanced fibre composites**
Edited by G. M. Hodgkinson
- 15 **Integrated design and manufacture using fibre-reinforced polymeric composites**
Edited by M. J. Owen and I. A. Jones
- 16 **Fatigue in composites**
Edited by B. Harris
- 17 **Green composites**
Edited by C. Baillie
- 18 **Multi-scale modelling of composite material systems**
Edited by C. Soutis and P. W. R. Beaumont
- 19 **Lightweight ballistic composites**
Edited by A. Bhatnagar
- 20 **Polymer nanocomposites**
Y-W. Mai and Z-Z. Yu

- 21 **Properties and performance of natural-fibre composite**
Edited by K. Pickering
- 22 **Ageing of composites**
Edited by R. Martin
- 23 **Tribology of natural fiber polymer composites**
N. Chand and M. Fahim
- 24 **Wood-polymer composites**
Edited by K. O. Niska and M. Sain
- 25 **Delamination behaviour of composites**
Edited by S. Sridharan
- 26 **Science and engineering of short fibre reinforced polymer composites**
S-Y. Fu, B. Lauke and Y-M. Mai
- 27 **Failure analysis and fractography of polymer composites**
E. S. Greenhalgh
- 28 **Management, recycling and reuse of waste composites**
Edited by V. Goodship
- 29 **Materials, design and manufacturing for lightweight vehicles**
Edited by P. K. Mallick
- 30 **Fatigue life prediction of composites and composite structures**
Edited by A. P. Vassilopoulos
- 31 **Physical properties and applications of polymer nanocomposites**
Edited by S. C. Tjong and Y-W. Mai
- 32 **Creep and fatigue in polymer matrix composites**
Edited by R. M. Guedes
- 33 **Interface engineering of natural fibre composites for maximum performance**
Edited by N. E. Zafeiropoulos
- 34 **Polymer-carbon nanotube composites**
Edited by T. McNally and P. Pötschke
- 35 **Non-crimp fabric composites: Manufacturing, properties and applications**
Edited by S. V. Lomov
- 36 **Composite reinforcements for optimum performance**
Edited by P. Boisse
- 37 **Polymer matrix composites and technology**
R. Wang, S. Zeng and Y. Zeng
- 38 **Composite joints and connections**
Edited by P. Camanho and L. Tong
- 39 **Machining technology for composite materials**
Edited by H. Hocheng
- 40 **Failure mechanisms in polymer matrix composites**
Edited by P. Robinson, E. S. Greenhalgh and S. Pinho
- 41 **Advances in polymer nanocomposites: Types and applications**
Edited by F. Gao
- 42 **Manufacturing techniques for polymer matrix composites (PMCs)**
Edited by S. Advani and K-T. Hsiao
- 43 **Non-destructive evaluation (NDE) of polymer matrix composites: Techniques and applications**
Edited by V. M. Karbhari
- 44 **Environmentally friendly polymer nanocomposites: Types, processing and properties**
S. S. Ray
- 45 **Advances in ceramic matrix composites**
Edited by I. M. Low
- 46 **Ceramic nanocomposites**
Edited by R. Banerjee and I. Manna

-
- 47 **Natural fibre composites: Materials, processes and properties**
Edited by A. Hodzic and R. Shanks
- 48 **Residual stresses in composite materials**
Edited by M. Shokrieh
- 49 **Health and environmental safety of nanomaterials: Polymer nanocomposites and other materials containing nanoparticles**
Edited by J. Njuguna, K. Pielichowski and H. Zhu
- 50 **Polymer composites in the aerospace industry**
Edited by P. E. Irving and C. Soutis
- 51 **Biofiber reinforcement in composite materials**
Edited by O. Faruk and M. Sain
- 52 **Fatigue and fracture of adhesively-bonded composite joints: Behaviour, simulation and modelling**
Edited by A. P. Vassilopoulos
- 53 **Fatigue of textile composites**
Edited by V. Carvelli and S. V. Lomov
- 54 **Wood composites – from nanocellulose to superstructures**
Edited by M. Ansell
- 55 **Toughening mechanisms in composite materials**
Edited by Q. Qin and J. Ye
- 56 **Advances in composites manufacturing and process design**
Edited by P. Boisse
- 57 **Structural integrity and durability of advanced composites**
Edited by P.W.R. Beaumont, C. Soutis and A. Hodzic
- 58 **Recent advances in smart self-healing polymers and composites**
Edited by G. Li and H. Meng

Preface

In the past several decades, the desire for lighter, tougher, stronger, and smarter materials in transportation vehicles, energy production, storage, and transport, military equipment and vehicles, infrastructure, chemical processing equipment, offshore oil and gas platforms, and consumer goods, has driven the use of fiber-reinforced polymer composite materials and polymeric coatings on metallic substrate. Fiber-reinforced polymer composite materials, while they have high specific strength, stiffness, corrosion resistance, and design tailorability, are prone to damage due to the various weak interfaces. Therefore, damage self-healing in polymer composite materials and coatings has been a topic of intensive research over the past two decades. The literature (papers, books, patents) has been growing exponentially. For people who are new to this area, it is difficult to digest the vast volume of literature, particularly when this literature is scattered in various types of journals, conference proceedings, and patents in various languages. Therefore, we feel that there is a need to have a one-stop shopping place so that newcomers and long-time engineers can easily get an overview of the historical backgrounds, on-going activities, and future perspectives in this emerging area of study. To this end, we invited a group of leading experts in various aspects of self-healing polymers and composites to contribute to this edited book. Owing to the time constraints and our limitations in knowledge, we must mention that this book is by no means comprehensive. Some relevant materials may have been overlooked, although that was not our intention.

This book consists of 12 chapters. Guoqiang Li and Harper Meng provide an overview of crack self-healing in polymer composite materials in Chapter 1. Using in-service (under stress, at low temperature, fixed boundary condition, etc.) load-bearing composite structures as an example, a set of evaluation criteria are proposed and the various healing schemes, including both intrinsic and extrinsic schemes, are compared against the criteria. The common requirement for any self-healing scheme to work is to bring fracture surfaces in contact. This requirement is emphasized using the strategy introduced in this chapter. Attention is then paid to healing structural-length scale cracks or wide-open cracks using a biomimetic two-step close-then-heal (CTH) strategy. Future perspectives such as combining hybrid intrinsic and extrinsic self-healing schemes, using artificial muscles, and employing hybrid artificial muscles and shape memory polymer fibers, are discussed. We believe that this chapter will provide an overall picture of the various self-healing schemes, challenges, and potential strategies to deal with the challenges.

After this introductory chapter by the two editors, we start with modeling of self-healing composite materials. Amir Shojaei in Chapter 2 covers the recent theoretical developments in the field of continuum damage-healing mechanics of self-healing materials. The mechanisms associated with the damage and healing are utilized to

propose the damage and healing parameters. The evolution laws for the damage and healing processes are developed within the continuum damage healing mechanics (CDHM) framework, which are calibrated in accordance with the experimentally measurable properties such as changes in the elastic moduli. We feel that this chapter will provide the skill set needed in modeling damage healing behavior.

In Chapter 3, Frank Jones and Russell Varley present solid-state healing of resins and composites. Solid-state healing represents a unique field of self-healing materials research characterized by the use of solid-state additives that impart inherent healing functionality to a given polymer matrix. As healing generally requires external intervention or activation, these systems are often referred to as mendable resin systems, but confer several advantages compared to other mechanisms. Some of these advantages are that healing is typically repeatable; able to repair damage to the same location time and again yet remaining indefinitely dormant until required. They are also convenient to incorporate into traditional fabrication technologies, enhancing their potential commercial application. Both one-phase and two-phase solid-state healing processes are discussed. Healing of fiber-reinforced polymer composites are also explored. We are optimistic that this chapter will provide our readers with critical knowledge and skills on successfully implementing healing by a solid healing agent.

Extrinsic self-healing by microcapsules is one of the most popular strategies in the literature. It is also one of the first strategies, if not the first scheme, to do damage self-healing. Dong Yu Zhu, Min Zhi Rong, and Ming Qiu Zhang provide a comprehensive review of microcapsule-based self-healing composite in Chapter 4. The review discusses the recent progress in this field from the viewpoint of material design and preparation. The challenges and future research opportunities are summarized at the end of the chapter. We believe that readers of this chapter will be provided with a grasp of the achievements to date and an insight into the future development in this fast growing field.

Christopher Hansen focuses on microvascular-based self-healing materials in Chapter 5. Inspired by the repair functionality of biological systems, self-healing by microvascular components is an approach to directly mimic the autonomic healing abilities of biological organisms. In this chapter, biological microvascular systems are briefly reviewed with respect to key design elements and considerations for functional and reliable synthetic microvascular systems. Fabrication using both subtractive and additive manufacturing techniques is discussed. The self-healing efficacy in terms of restoration of mechanical strength is evaluated. It is envisioned that the field of microvascular self-healing has significant potential for continued growth.

As an intrinsic self-healing strategy, reversible chemical bonds have been widely studied. In Chapter 6, Pengfei Du and Xinling Wang focus on reversible cross-linking polymer-based self-healing materials. They start with reviewing the autonomous self-healing polymers with embedded microencapsulated healing agent. They then focus on the cross-linked healable polymeric materials based on reversible noncovalent bonds, including hydrogen bonds, π - π stacking interaction, and metal-ligand coordination. Finally, they review the cross-linked healable polymeric material containing

reversible covalent bonds (DA adducts). We believe that this healing scheme will help eliminate hidden hazards, prolong service life, and expand the application area of polymeric materials.

Supramolecule chemistry is another fast-growing area in the intrinsic self-healing field. Wenwen Deng, Yang You, and Anqiang Zhang focus on supramolecular network-based self-healing polymer materials in Chapter 7. Supramolecular polymers could form a dynamic network, which exhibits the ability to heal their damages. In this chapter, some recent advances in supramolecule self-healing materials based on noncovalent interactions, including hydrogen bonding, π - π stacking, metal-ligand complexes, and ionomers, are discussed. Furthermore, the self-healing properties and self-healing mechanisms of these materials are described. In addition, the challenges and future perspectives are discussed. We believe that this chapter provides fundamental knowledge on this emerging research area.

Chapter 8 focuses on self-healing coatings. Corrosion of metallic structures has been a challenging problem for centuries. Coatings with polymers have been popular in recent decades but suffer from damage in the coating layer. A.E. Hughes addresses this issue by developing self-healing polymeric coatings. In this chapter, a wide variety of self-healing approaches to coatings is investigated. Other healing mechanisms that have potential applications in coatings are also explored. A broad range of coating applications are discussed with particular attention to coatings where the polymer acts as the resin or binder. We believe that self-healing coatings represent considerable opportunities for future research and development. We envision that applications to real-world structures will become available in the foreseeable future.

Except for a limited number of healing systems, most intrinsic and extrinsic self-healing systems need some external help such as heating to increase the mobility of molecules so that molecular interaction can occur. For these systems, like human skin, the damage needs to be sensed before healing occurs. In Chapter 9, Simon Hayes, Timothy Swait, and Austin Lafferty discuss self-sensing and self-healing in composites. They introduce the principles of self-sensing, both optically and electrically, and show in each case how the sensor utilizes the reinforcing fibers of the composite in order to determine the damage state. Intrinsic self-healing is then discussed, presenting different ways of incorporating a self-healing response into resins that are suitable for use as matrix materials for composites. Strategies for combining electrical self-sensing with systems requiring thermal activation and optical self-sensing with those requiring optical activation are discussed. We believe that self-sensing will have a significant impact on enhancing the self-healing systems, particularly on extrinsic self-healing systems.

As a comparatively new member in the self-healing family, self-healing of shape memory polymers or self-healing of conventional nonshape memory polymers by shape memory effect has been intensively studied by several groups in the past several years. In this book, we devote three chapters to this emerging research field.

In Chapter 10, Haibao Lu, Wei Min Huang, Zhen Ding, Chang Chun Wang, Hai Po Cui, Cheng Tang, Jun Wei, Yong Zhao, and Cheng Li Song focus on rubber-like polymeric shape memory hybrids with repeatable heat-assisted self-healing and joule

heating functions. The fabricated hybrids are not only rubber-like from above to below their shape recovery temperature, but also have repeatable heat-assisted self-healing functionality. By incorporation of carbon blacks in the polymer matrix, the hybrids maintain highly elastic, and are able to be directly joule heated for shape recovery. The major parameters, which affect the performance of the hybrids, are experimentally investigated in a systematic manner. We are confident that this chapter will deepen understanding and enhance application of shape memory assisted self-healing in rubber-like hybrid polymers.

In Chapter 11, Gefu Ji, Pengfei Zhang, Jones Nji, Manu John, and Guoqiang Li focus on self-healing of impact induced cracks in rigid and stiff thermosetting shape memory polymer matrix. Several fiber-reinforced thermosetting shape memory polymer structures, including composite sandwich structures, grid-stiffened composite structures, and 3-D woven fabric-reinforced composite structures, are fabricated, low-velocity impact tested, and healed per the biomimetic CTH scheme. Several impact-healing cycles are conducted to demonstrate the healing repeatability. Repeated damage sensing by a percolated carbon nanotube network is also presented. It is validated that the CTH scheme can heal structural-length scale crack in fiber-reinforced thermosetting shape memory polymer composite structures repeatedly, efficiently, timely, and have potential to heal autonomously.

In Chapter 12, Harper Meng, Pengfei Zhang, Oludayo Ajisafe, and Guoqiang Li further show that structural-length scale cracks in conventional thermosetting polymers, which do not have shape memory effect, can be repeatedly healed by embedding a small amount of prestretched shape memory polymer fibers and thermoplastic healing agent. Shape memory polymer fibers in 1-D, 2-D, and 3-D configurations are investigated. Specimens with both free boundary conditions and fixed boundary conditions are tested, which confirms that tensile-stressed specimens or specimens under in-service conditions can also be repeatedly healed with proper programming of the shape memory polymer fibers. We believe that this study provides a new and cost-effective way of repeatedly healing wide-open cracks in conventional thermosetting polymer composite structures.

The guest editors of this edited book are confident that this collection of highly relevant and impactful contributions will be of interest to many diverse audiences, be they in academia or industry. We are grateful to have achieved such a high-quality collection of chapters and would like to thank the authors for their contributions. We would also like to thank the Woodhead Team for their assistance during the course of organizing this book. We would like to encourage the whole field to continue the progress in all fronts related to self-healing polymers and composites.

*Guoqiang Li, Ph.D.
Harper Meng, Ph.D.*

Contents

List of contributors	ix
Woodhead Publishing Series in Composites Science and Engineering	xi
Preface	xv
1 Overview of crack self-healing	1
<i>G. Li, H. Meng</i>	
1.1 Review of existing self-healing systems	1
1.2 Future research opportunities	11
1.3 Concluding remarks	14
Acknowledgments	15
References	15
2 Modeling of self-healing smart composite materials	21
<i>A. Shojaei</i>	
2.1 Introduction	21
2.2 Finite deformation kinematics: elastic, plastic, damage, and healing in polymers	24
2.3 Plastic deformation in polymers	27
2.4 Continuum damage and healing mechanics	30
2.5 Physically consistent evolution laws for the damage and healing processes	39
2.6 Concluding remarks	48
References	48
3 Solid-state healing of resins and composites	53
<i>F.R. Jones, R.J. Varley</i>	
3.1 Introduction	53
3.2 Diffusional solid-state healing	54
3.3 Two-phase solid-state healing	80
3.4 Smart composites	95
3.5 Conclusions	96
References	96
4 Microcapsule-based self-healing materials	101
<i>D.Y. Zhu, M.Z. Rong, M.Q. Zhang</i>	
4.1 Introduction	101
4.2 Microencapsulation techniques	105
4.3 Healing chemistries	112

4.4	Conclusions	122
	Acknowledgments	122
	References	122
5	Microvascular-based self-healing materials	129
	<i>C.J. Hansen</i>	
5.1	Introduction to microvascular-based self-healing	129
5.2	Biological inspiration for microvascular self-healing systems	130
5.3	Design of microvascular self-healing systems	132
5.4	Fabrication of embedded microvascular structures	140
5.5	Applications, performance, and assessment of microvascular-based self-healing	145
5.6	Future directions for microvascular-based self-healing	151
5.7	Resources for further information	152
	References	152
6	Reversible cross-linking polymer-based self-healing materials	159
	<i>P. Du, X. Wang</i>	
6.1	Introduction	159
6.2	Autonomically self-healing polymeric materials	160
6.3	Healable polymeric materials	162
6.4	Prospects	174
	References	175
7	Supramolecular network-based self-healing polymer materials	181
	<i>W. Deng, Y. You, A. Zhang</i>	
7.1	Introduction	181
7.2	Self-healing supramolecular polymers based on hydrogen bonds	181
7.3	Self-healing supramolecular polymers based on π - π stacking interactions	193
7.4	Self-healing supramolecular polymers based on metal-ligand interactions	198
7.5	Self-healing ionomers	202
7.6	Summary and outlook	204
	References	204
8	Self-healing coatings	211
	<i>A.E. Hughes</i>	
8.1	Introduction	211
8.2	General definitions of self-healing	215
8.3	Coatings versus other polymer applications	217
8.4	Polymer healing mechanisms adopted for coatings	220
8.5	Functional recovery in coating applications	227
8.6	The marriage of polymer healing and functional repair	230
8.7	Conclusions	231
	Acknowledgment	231
	References	231