FIFTH INTERNATIONAL CONFERENCE ON
SELF-HEALING MATERIALS
JUNE 22-24, 2015
CONFERENCE PROGRAM

PROGRAM SPONSORED
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Dear Colleagues:

The Executive Organizing Committee and the City Of Durham welcome you to the Fifth International Conference on Self-Healing Materials (ICSHM2015), co-hosted by Duke University, North Carolina State University, the University of North Carolina - Chapel Hill, and North Carolina Central University.

We deeply appreciate the generous sponsorship of the four co-hosting universities, the Netherlands Enterprise Agency, Eastman Chemical Company, Lord Corporation, the National Science Foundation, the National Institutes of Health, the Air Force Office of Scientific Research, and the Soft Matter Journal of the Royal Society of Chemistry. We also thank RILEM -- the International Union of Laboratories and Experts in Construction Materials, Systems and Structures -- for promoting with ICSHM2015 to their membership.

We have an exciting program that consists of over 230 abstracts submitted from nineteen different countries and features six plenary speakers, three keynote speakers, 32 oral sessions and two poster sessions. The topics include the traditional self-healing cements, polymers, composites, coatings and paints, metals, ceramics and modeling. For the first time, the program also includes sessions on self-healing biomaterials and hydrogels.

The Durham Convention Center is located in the heart of downtown Durham and all are invited to partake in the many and varied clubs and restaurants within easy walking distance. Please refer to the promotional information contained within the conference bag or go online to http://www.durham-nc.com/things-to-do/.

Welcome to Durham - North Carolina’s Bull City!

Sincerely;

ICSHM2015 Executive Organizing Committee and the City of Durham
Registration/Information Desk Hours

Sunday, June 21, 2015

5:00 pm – 8:00 pm – Conference Materials Pick Up

Monday, June 22, 2015

7:30 am – 8:30 am – Conference Materials Pick Up
12:30 pm – 1:30 pm
5:00 pm – 6:00 pm

Tuesday, June 23, 2015

7:30 am – 8:30 am
12:30 pm – 1:30 pm
5:00 pm – 6:00 pm

Wednesday, June 24, 2015

7:30 am – 8:30 am
12:30 pm – 1:30 pm
Day-by-Day Program

Monday, June 22, 2015

7:45 am – 8:00 am  Welcome and Call to Order  
Jr. Ballroom B

8:00 am – 9:00 am  Plenary Session I – Jr. Ballroom B  
Self-healing Concrete: Paving the Way for Application in Practice  
Nele De Belie  
Magne Lab for Concrete Research  
Department of Structural Engineering  
Ghent University

9:15 am – 10:30 am  FOUR CONCURRENT SESSIONS

I. Biomaterials I – Jr. Ballroom A1  
Chair: Niels Holten-Anderson, Massachusetts Institute of Technology

9:15 am – 9:45 am  BIOM 01-272 KEYNOTE: Targeting Failure Mechanisms with Self-Healing Strategies  
L. D. Timmie Topoleski, University of Maryland, Baltimore

9:45 am – 10:00 am  BIOM 02-241 Fracture Characterization of Self-Healing Dental Composites  
Michael Keller, The University of Tulsa

10:00 am – 10:15 am  BIOM 03-267 Soft, Stretchable, and Self-Healing Liquid Metals  
Michael Dickey, NC State University

10:15 am – 10:30 am  BIOM 04-7 Catalyst-Free Self-Healing Bone Cement  
Monty Reichert, Duke University

II. Cementitious Materials I – Jr. Ballroom B  
Chair: Tony Jefferson, Cardiff University

9:15 am – 9:30 am  CEMT 01-177 Effect of Carbonation on Autogenous Self-Healing in Cementitious Materials  
Haoliang Huang, Delft University of Technology
Monday, June 22, 2015

9:30 am – 9:45 am  CEMT 02-75 Elucidation of Rapid Reduction Mechanism of Water Flow through Concrete Crack Regarded as Self-healing Phenomenon Prof. Toshiharu Kishi, The University of Tokyo

9:45 am – 10:00 am  CEMT 03-261 Effects of GGBS Content on Self-Healing of Engineered Cementitious Composites En-Hua Yang, Nanyang Technological University

10:00 am – 10:15 am  CEMT 04-166 Influence of Fly Ash Type on Mechanical and Self-Healing Behavior of Engineered Cementitious Composite (ECC) Shunzhi Qian, Nanyang Technological University

10:15 am – 10:30 am  CEMT 05-276 Self-Healing of High Performance Fiber-Reinforced Cementitious Composites Ömer Kaya, Istanbul Technical University

III. Thermoplastics & Thermosets I – Jr. Ballroom A2
Chair: Darlene Taylor, North Carolina Central University


9:30 am – 9:45 am  THRM 02-210 Thermally-Healable Crosslinked Epoxidized Natural Rubber Sophie Norvez, ESPCI ParisTech

9:45 am – 10:00 am  THRM 03-158 Tough Elastomers by Hybridizing Covalent and Reversible Networks Jinrong Wu, Harvard University

10:00 am – 10:15 am  THRM 04-186 Chelation-Assisted CuAAC of Star-Shaped Polymers Enables Fast Self-Healing at Low Temperatures Steve Neumann, Martin-Luther-University Halle-Wittenberg

10:15 am – 10:30 am  THRM 05-285 Enhancing Mechanical Performance of a Covalent Self-Healing Material by Sacrificial Non-Covalent Bonds James Neal, University of California, Irvine
Monday, June 22, 2015

Chair: Wataru Nakao, Yokohama National University

9:15 am – 9:30 am  **CM+MT O1-155** On the Decomposition Behaviour of MoSi2 and B-Doped MoSi2 Sacrificial Particles in Self Healing Yttria Stabilized Zirconia Coating
A. L. Carabat, Delft University of Technology

9:30 am – 9:45 am  **CM+MT O2-71** Cyclic Thermogravimetry Analysis of Ceramic-Intermetallic Composites Prepared by SPS for a New Self-Healing TBC
Nozahic Franck, INPT-CIRIMAT-ENSIACET

9:45 am – 10:00 am  **CM+MT O3-145** Selection of Mn+1AXn-Phase Ceramics for Autonomous Healing of Crack Damage
Ann-Sophie Farle, Delft University of Technology

10:00 am – 10:15 am  **CM+MT O4-245** Durability Evaluation of Alumina/ SiC Self-Healing Composite Ceramics as a Function of Internal Oxidation Layer Thickness
Shunsuke Yoshioka, Yokohama National University

10:15 am – 10:30 am  **CM+MT O5-192** New Healing Agents for High Temperature Alumina Ceramics Delivering Mixed Oxides
Shunsuke Yoshioka, Yokohama National University

11:00 am – 12:15 pm  **FOUR CONCURRENT SESSIONS**

I. Biomaterials II – Jr. Ballroom A1
Chair: Shyni Varghese, University of California, San Diego

11:00 am – 11:30 am  **BIOM O5-48** KEYNOTE: Self-Healing Chemistry and Electronic Applications
Zhenan Bao, Stanford University

11:30 am – 11:45 am  **BIOM O6-204** Regulation of Self-Healing Hydrogels for Sequential Cell Attachment and Detachment
Yong Wang, The Pennsylvania State University
Monday, June 22, 2015

11:45 am – 12:00 pm  **BIOM 07-115** A Novel Wound Dressing based on Ag/Zwitterionic Polymer Hydrogel
Amin GhavamiNejad, Chonbuk National University

12:00 pm – 12:15 pm  **BIOM 08-289** Supramolecular Transient Networks in Water: from Hydrogels to Biomedical Applications
Patricia Y. W. Dankers, Eindhoven University of Technology

**II. Cementitious Materials II – Jr. Ballroom B**
Chair: Amy Peterson, Worcester Polytechnic Institute

11:00 am – 11:15 am  **CEMT 06-153** Sodium Silicate Particles Encapsulated in Epoxy Resin for Self-Healing Cement-based Materials
Hua Dong, Delft University of Technology

11:15 am – 11:30 am  **CEMT 07-82** Self-Healing of Cementitious Composites via Pelletisation of Mineral Admixtures
Rami Alghamri, University of Cambridge

11:30 am – 11:45 am  **CEMT 08-256** Cementitious Materials with Mineral Additions: Impact on the Self-Healing Kinetics and the Products Formation
Kelly Olivier, Université Paris-Saclay

11:45 am – 12:00 pm  **CEMT 09-73** Influence of Expansive Minerals on the Self-Healing of Cement Paste and Mortar Systems
Tanvir Qureshi, University of Cambridge

12:00 pm – 12:15 pm  **CEMT 010-100** Encapsulated Mineral Precursors for Self-Healing Cement based Composites
Antonios Kanellopoulos, University of Cambridge

**III. Thermoplastics & Thermosets II – Jr. Ballroom A2**
Chair: Nancy Sottos, University of Illinois

11:00 am – 11:15 am  **THRM 06-228** Renewable Furan-based Epoxy Systems for Self-Healing Applications
Giuseppe Palmese, Drexel University
Monday, June 22, 2015

11:15 am – 11:30 am  **THRM 07-174** Self-Healing Polymers based on the (Retro)-Diels-Alder Reaction: Tuning the Healing Temperature
Martin D. Hager, Friedrich Schiller University Jena

11:30 am – 11:45 am  **THRM 08-50** Self-Healable and Recyclable Crosslinked Polymer via Disulfide Metathesis Reaction
Min Zhi Rong, Sun Yat-Sen University

11:45 am – 12:00 pm  **THRM 09-41** Thermo-Reversibly Cross-Linked Rubber Compounds
Lorenzo Massimo Polgar, University of Groningen

12:00 pm – 12:15 pm  **THRM 010-216** Thermal and Rheological Characterization of Diels-Alder based Reversible and Mixed Reversible/Irreversible Networks
Maria Mercedes Diaz Acevedo, Vrije Universiteit Brussel

**IV. Ceramics & Metals II – Jr. Ballroom A3**
Chair: Wim Sloof, Delft University of Technology

11:00 am – 11:15 am  **CM+MT 06-61** Self Healing of Creep Damage in Fe-Au and Fe-Au-B-N Alloys
Sybrand van der Zwaag, Delft University of Technology

11:15 am – 11:30 am  **CM+MT 07-110** Self-Healing of Multifunctionality in Metal/Oxide Hybrid Materials
Makoto Nanko, Nagaoka University of Technology

11:30 am – 11:45 am  **CM+MT 08-187** Model-based Design of Self-Healing Creep Steels
Casper Versteylen, Delft University of Technology

11:45 am – 12:00 pm  **CM+MT 09-243** Application Road Map of Self-Healing Ceramics
Wataru Nakao, Yokohama National University

12:00 pm – 12:15 pm  **CM+MT 010-215** High Temperature Oxidation Induced Healing of Pre-erosion Cracks in Cr2AlC MAX Phase Ceramic Surfaces
Lu Shen, Delft University of Technology
Monday, June 22, 2015

1:45 pm – 2:45 pm  
Plenary Session II – Jr. Ballroom B  
Molecular Basis of Self-Healing in Wet Biological Adhesives and Their Synthetic Mimics  
Phil Messersmith  
Departments of Bioengineering and Materials Science & Engineering  
University of California, Berkeley

3:00 pm – 4:15 pm  
FOUR CONCURRENT SESSIONS

Chair: Phil Messersmith, University of California, Berkeley

3:00 pm – 3:30 pm  
**BIOI 01-273** KEYNOTE: Bio-Inspired Metal-Coordination: Using More of Nature’s Tricks to Assemble Bio-Materials with Multi-Functional Properties  
Niels Holten-Andersen, Massachusetts Institute of Technology

3:30 pm – 3:45 pm  
**BIOI 02-56** Mussel-Inspired Self-Healing Metallopolymers  
Martin D. Hager, Friedrich Schiller University Jena

3:45 pm – 4:00 pm  
**BIOI 03-102** Effect of Different Curing Agents on the Fracture Behavior of Epoxy-Shelled Bio-Microcapsule Under Stress  
Guangming Zhu, Shenzhen University

4:00 pm – 4:15 pm  
**BIOI 04-251** Bio-Inspired Stimuli Responsive Reversible Actuation for Selective Growth  
Richard S. Trask, University of Bristol

II. Cementitious Materials III – Jr. Ballroom B  
Chair: Victor Li, University of Michigan

3:00 pm – 3:15 pm  
**CEMT 011-164** Can Repeatable Self-Healing Be Achieved in Cementitious Materials?  
Mo Li, University of Houston

3:15 pm – 3:30 pm  
**CEMT 012-253** Capsules Changing in Brittleness Due to Leaching of Plasticizing Agents  
Kim Van Tittelboom, Magnel Laboratory for Concrete Research
Monday, June 22, 2015

3:30 pm – 3:45 pm  CEMT O13-190 Materials for Life (M4L): Combining Multi-Scale Healing Techniques in Cementitious Materials
Robert Davies, Cardiff University

3:45 pm – 4:00 pm  CEMT O14-281 Microscopical Characterization of the Self Healing Mechanisms in High Performance Cementitious Composites Reinforced with Steel
Liberato Ferrara, Politecnico di Milano

4:00 pm – 4:15 pm  CEMT O15-74 Detailed Observation of Air Bubble Generation by Water Flow Hydrodynamics in Narrow Gaps such as Concrete Cracks
Kayondo Muzafalu, The University of Tokyo

III. Mechanochemistry – Jr. Ballroom A2
Chair: Steve Craig, Duke University

3:00 pm – 3:15 pm  MECH O1-230 Mechanochemistry in Glassy Polymers: Experiments and Simulations on Spiropyran-linked Poly(methyl methacrylate)
Meredith Silberstein, Cornell University

3:15 pm – 3:30 pm  MECH O2-242 Mechanochromism of Diarylbibenzofuranone-based Dynamic Covalent Polymers
Hideyuki Otsuka, Tokyo Institute of Technology

3:30 pm – 3:45 pm  MECH O3-57 Mechanochemical Pyramidalization of Alkynes
Charles E. Diesendruck, Technion – Israel Institute of Technology

3:45 pm – 4:00 pm  MECH O4-212 Design of Mechanochemically Active Interfaces
Meenakshi Sundaram, Cornell University

4:00 pm – 4:15 pm  MECH O5-46 Development of Latent Mechanocatalyst for Copper(I)-Catalyzed Azide/Alkyne “Click” Reactions
Philipp Michael, Martin-Luther-Universitat Halle-Wittenberg

Chair: Zhenan Bao, Stanford University
Monday, June 22, 2015

3:00 pm – 3:15 pm  CHAR 01-98 A Nonlinear Fracture Mechanics Approach to the Assessment of the Interfacial Healing in Self-Healing Elastomers
A. M. Grande, Delft University of Technology

3:15 pm – 3:30 pm  CHAR 02-175 Neutron Scattering Investigation of a Covalent/Non-Covalent Self-Healing Polymer
Wim Pyckhout-Hintzen, Forschungszentrum Juelich

3:30 pm – 3:45 pm  CHAR 03-167 Tracing Self-Healing Through Raman Spectroscopy and Micro-CT
Mo Li, University of Houston

3:45 pm – 4:00 pm  CHAR 04-259 Microscopic Healing Evaluation on Reversible Covalent Polymer Network Systems
Joost Brancart, Vrije Universiteit Brussel

4:00 pm – 4:15 pm  CHAR 05-87 Magnetically Triggered Crack Healing of Bituminous Materials
Jeoffroy Etienne, Swiss Federal Laboratories for Materials Science and Technology EMPA / Swiss Federal Institute of Technology in Zurich ETHZ

4:30 pm – 6:30 pm  Poster Session I – Jr. Ballroom C
  - Bacteria-based Cementitious Materials
  - Cementitious Materials
  - Microcapsules: Cementitious
**Tuesday, June 23, 2015**

7:45 am – 8:00 am  Brief Announcements and Call to Order – Jr. Ballroom B

8:00 am – 9:00 am  Plenary Session III – Jr. Ballroom B
Mechanofunctional Polymers: Luminescent Probes & Catalytic Triggers
Rint Sijbesma
Department of Chemical Engineering and Chemistry
Eindhoven University of Technology

9:15 am – 10:30 am  FOUR CONCURRENT SESSIONS

**I. Supramolecular Polymers I – Jr. Ballroom A1**
Chair: Rint Sijbesma, Eindhoven University of Technology

9:15 am – 9:30 am  **SUPR O1-47** Relationship Between the Network Relaxation Time and Supramolecular Self-Assembly Time and the Healing Kinetics in Ionomers
Ranjita K. Bose, Delft University of Technology

9:30 am – 9:45 am  **SUPR O2-95** Interactions Between Supramolecular Self-Healing Polymers and Inorganic Reinforcements
Federica Sordo, Ecole Polytechnique Fédérale de Lausanne

9:45 am – 10:00 am  **SUPR O3-189** Polybutylene Oxide Model Polymers with Hydrogen Bonds
Jurgen Allgaier, Forschungszentrum Juelich

10:00 am – 10:15 am  **SUPR O4-146** Self-Healing via "Click"-based Concepts and Supramolecular Principles
Wolfgang Binder, Martin-Luther University Halle-Wittenberg

10:15 am – 10:30 am  **SUPR O5-111** A Thermoreversible Supramolecular Polyurethane Capable of Highly Efficient Healing at 45 °C
Antonio Feula, University of Reading

**II. Cementitious Materials IV – Jr. Ballroom B**
Chair: Mo Li, University of Houston
9:15 am – 9:30 am  **CEMT 016-218** Investigation of Self-Healing Rebar Coatings for Reinforced Concrete
Amy M. Peterson, Worcester Polytechnic Institute

9:30 am – 9:45 am  **CEMT 017-63** Shape Memory Polymer (SMP) Prestressing System to Enhance the Autogenous Healing of Structural Concrete
Oliver Teall, Cardiff University

9:45 am – 10:00 am  **CEMT 018-54** Smart Superabsorbent Polymers for Self-Sealing and Healing of Mortar
Arn Mignon, University of Ghent

10:00 am – 10:15 am  **CEMT 019-148** Evaluation of the Self-Sealing Effect of Mortar Containing Polymeric Healing Agents
Gruyaert Elke, Ghent University

10:15 am – 10:30 am  **CEMT 020-31** Autogenous Healing of Cementitious Materials Promoted by Superabsorbent Polymers Studied by Means of X-ray Microtomography
Didier Snoeck, Magnel Laboratory for Concrete Research

**III. Microcapsules: Polymers I – Jr. Ballroom A2**
Chair: Michael Keller, The University of Tulsa

9:15 am – 9:30 am  **MCAP-POLY 01-34** Recovery of Mechanical and Electrical Properties in Conductive Self-Healing Polymer Composite Coatings
Brennan Bailey, École Polytechnic Fédéral de Lausanne

9:30 am – 9:45 am  **MCAP-POLY 02-58** pH-Dependent Switchable Permeability from Core-Shell Microcapsules
Joshua M. Grolman, University of Illinois at Urbana-Champaign

9:45 am – 10:00 am  **MCAP-POLY 03-201** Screening Barrier Properties of Double Shell Walled Microcapsules for Self-Healing Composite Materials
Siddharth Dev, University of Massachusetts Lowell
10:00 am – 10:15 am  **MCAP-POLY 04-239** Microcapsule-based Healing of Shape Memory Polymers
Christopher J. Hansen, University of Massachusetts Lowell

10:15 am – 10:30 am  **MCAP-POLY 05-51** Microfluidic Fabrication of Microcapsules Encapsulating Mineral Oil and Evaluation of Self-healing of Self-cleaning Performance
Hyeong Jin Jeon, Pusan National University

**IV. Coatings & Paints – Jr. Ballroom A3**
Chair: Gerald Wilson, Autonomic Materials, Inc.

9:15 am – 9:30 am  **COAT 01-42** Interfacial Healing of Hybrid Sol-gel based Polymers Containing Thermo-reversible Tetra-sulphide Groups
Mina Abdolahzadeh, Delft University of Technology

9:30 am – 9:45 am  **COAT 02-181** Acrylate-based UV-cured Self-replenishing Hydrophobic Coatings for Further Industrial Applications
Yujing Zhang, Eindhoven University of Technology

9:45 am – 10:00 am  **COAT 03-91** Use of Confocal Raman and Localized Electrochemical Methods to Study Multiple Self-Healing Actions in Corrosion Protection Coating
Herman Terryn, Vrije Universiteit Brussel

10:00 am – 10:15 am  **COAT 04-104** Effect of the Stoichiometry on the Healing Capability of an Aromatic-Aliphatic Polyetherimide.
Arijana Susa, Delft University of Technology

10:15 am – 10:30 am  **COAT 05-152** Poly(ethylene glycol)-based Hydrophilic Networks: Model Study Towards Self-replenishing Lubricious Coatings
Peter. T. M. Albers, Eindhoven University of Technology

11:00 am – 12:15 am  **FOUR CONCURRENT SESSIONS**

**I. Supramolecular Polymers II – Jr. Ballroom A1**
Chair: Zhibin Guan, University of California, Irvine
Tuesday, June 23, 2015

11:00 am – 11:15 am  **SUPR 06-55** Self-Healing Metallopolymers: Investigation of the Mechanism
Stefan Bode, FSU Jena

11:15 am – 11:30 am  **SUPR 07-196** New Self-healing Materials based on Mixtures of Poly(ionic liquids) and Bromobutyl Rubber
Marcus Suckow, Leibniz-Institut für Polymerforschung Dresden e. V.

11:30 am – 11:45 am  **SUPR 08-36** A Double Self-Healing System by Combination of Covalent Crosslinking via the CuAAC Click Reaction
Diana Doehler, Martin-Luther-Universität Halle-Wittenberg

11:45 am – 12:00 pm  **SUPR 09-205** Self-Healing Processes in Ionomeric Elastomers
Nico Hohlbein, Universität zu Köln

12:00 pm – 12:15 pm  **SUPR 010-203** π-π Stacked Healable Supramolecular Polymer Networks
Lewis Hart, University of Reading

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**II. Cementitious Materials V – Jr. Ballroom B**
Chair: Guangming Zhu, Shenzhen University

11:00 am – 11:15 am  **CEMT 021-220** Healing Quantification in Cementitious Materials using Nonlinear Coda Wave Modulation
Benoit Hilloulin, Ecole Centrale de Nantes

11:15 am – 11:30 am  **CEMT 022-81** Proof of Efficiency: Examination of Concrete Beams with Self-healing Properties by Non-destructive Testing Methods
Fabian Malm, Technical University Munich

11:30 am – 11:45 am  **CEMT 023-252** Experimental Study on Self-healing Effect Against Freeze/thaw Cycles of FRCC with PVA Fibers and Additives
Tomoya Nishiwaki, Tohoku University

11:45 am – 12:00 pm  **CEMT 024-231** Analysis of Self-Healing Potential of Advanced Cementitious Composites – Preliminary Compositions and Experimental Results
Cornelia Baeră, Technical University of Cluj-Napoca
Tuesday, June 23, 2015

12:00 pm – 12:15 pm  
**CEMT 025-136** Investigation on the Influence of Self-healing on ECC’s Tensile Mechanical Properties
Zhigang Zhang, Southeast University

Chair: L. D. Timmie Topoleski, University of Maryland, Baltimore County

11:00 am – 11:15 am  
**MCAP-POLY 06-208** Characterization of Solvent-based Self-healing in a Thermoplastic Toughened Epoxy Matrix
A. R. Jones, University of Illinois at Urbana-Champaign (UIUC)

11:15 am – 11:30 am  
**MCAP-POLY 07-72** Thermal Properties of Microcapsule-Reinforced Thermoset Polymers
Michael Keller, University of Tulsa

11:30 am – 11:45 am  
**MCAP-POLY 08-38** Self-healing Polymers Towards Fast Restoration of Strength
Ming Qiu Zhang, Sun Yat-sen University

11:45 am – 12:00 pm  
**MCAP-POLY 09-62** High Throughput Platform to make Microcapsules for Industrially Feasible Self-healing Systems
Seda Cakir, University of Ghent

12:00 pm – 12:15 pm  
**MCAP-POLY 010-37** Development of Microcapsules as Additives for Advanced Composites
Roberto Teixeira, Devan Chemicals

Chair: Santiago Garcia, Delft University of Technology

11:00 am – 11:15 am  
**COAT 06-246** Design and Characterization of Self-Healing Functionality in Protective Coatings
Dr. Gerald O. Wilson, Autonomic Materials, Inc.

11:15 am – 11:30 am  
**COAT 07-112** Stimuli-responsive Nanocapsules for Self-healing and Anticorrosion
Daniel Crespy, Max Planck Institute for Polymer Research
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<tr>
<th>Time</th>
<th>Session Title</th>
<th>Speaker(s)</th>
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</thead>
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<tr>
<td>11:30 am – 11:45 am</td>
<td><strong>COAT 08-283</strong> Controlled Release of Green-inhibitors Entrapped in Micro-Spheres (Inhibispheres™) for Corrosion Protection in Aerospace</td>
<td>Elisa Campazzi, Airbus Group SAS</td>
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<td>11:45 am – 12:00 pm</td>
<td><strong>COAT 09-213</strong> Synthesis and Characterization of Microcapsules for Self Healing Coatings</td>
<td>Vimal Saini, Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT</td>
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<td>12:00 pm – 12:15 pm</td>
<td><strong>COAT 010-227</strong> Self-Healing Anticorrosive Coatings via Microcapsules Containing UV Curable Epoxy Resin</td>
<td>Michael Odarczenko, University of Illinois</td>
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<td>1:45 pm – 2:45 pm</td>
<td><strong>Plenary Session IV – Jr. Ballroom B</strong> Tough and Self-healing Hydrogels based on Reversible Sacrificial Bonds</td>
<td>Jianping Gong, Hokkaido University</td>
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<td>3:00 pm – 4:15 pm</td>
<td><strong>THREE CONCURRENT SESSIONS</strong></td>
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<td>3:00 pm – 3:15 pm</td>
<td><strong>HYDR 01-269</strong> pH-responsive Self-healing Hydrogels</td>
<td>Shyni Varghese, University of California, San Diego</td>
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<td>3:15 pm – 3:30 pm</td>
<td><strong>HYDR 02-161</strong> Self-healing Nanostructured Colloidal Gelatin Gels for Bone Regeneration</td>
<td>Huanan Wang, SEAS, Harvard University</td>
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<td>3:30 pm – 3:45 pm</td>
<td><strong>HYDR 03-129</strong> Self-healing Hydrogels based on Non-covalent Calcium-bisphosphonate Interactions</td>
<td>Sander Leeuwenburgh, Radboud University Medical Center</td>
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Tuesday, June 23, 2015

3:45 pm – 4:00 pm  HYDR O4-29 Designing Extremely Resilient and Tough Hydrogels via Delayed Dissipation
Shaoting Lin, Massachusetts Institute of Technology

4:00 pm – 4:15 pm  HYDR O5-149 Formation of Self-Healing Colloidal Gels based on pH-induced Self-Assembly of Gelatin and Silica Nanoparticles
Mani Diba, Radboud University Medical Center

Chair: Erik Schlangen, Delft University of Technology

3:00 pm – 3:15 pm  MCAP-CEMT O1-130 Fully Monitoring of Fracture and Healing on Polymer and Concrete Systems: Towards an Autonomous Smart Sensing System
Pieter Minnebo, Free University of Brussels

3:15 pm – 3:30 pm  MCAP-CEMT O2-80 Self-healing of Cementitious Composites using Silica Precursors as Microencapsulated Healing Agents
Chrysoula Litina, University of Cambridge

3:30 pm – 3:45 pm  MCAP-CEMT O3-44 Investigation of Self-healing in Cementitious Materials with Sulfoaluminate Cement Microcapsules using X-ray Computed Tomography
Guohao Fang, Shenzhen University

3:45 pm – 4:00 pm  MCAP-CEMT O4-197 Production of Microcapsules for Self-healing Concrete using Microfluidics
Livia Souza, University of Cambridge

4:00 pm – 4:15 pm  MCAP-CEMT O5-138 The Microcapsule Responsive to Chloride Ion
Guangming Zhu, Shenzhen University

Chair: Etelvina Javierre, Centro Universitario de la Defensa

3:00 pm – 3:15 pm  MODL-CEMT O1-200 Finite Element Simulation of Cementitious Autogenous Healing with a new Thermo-hygro-chemical Model
A D Jefferson, Cardiff University
3:15 pm – 3:30 pm  **MODL-CEMT 02-90** Numerical Study of Self-healing Effect on Transport Properties in Cement Paste
Yun Zhang, Delft University of Technology

3:30 pm – 3:45 pm  **MODL-CEMT 03-266** Prediction of Strength Recovery Rate in Self-Healing Ceramics Using Oxidation Kinetics and Nonlinear Fracture Mechanics
Toshio Osada, National Institute for Materials Science

3:45 pm – 4:00 pm  **MODL-CEMT 04-132** A Numerical Model of the Transportation of Self-healing Agent in and around Concrete Discrete Cracks
Chuansan Ma, Cardiff University

4:00 pm – 4:15 pm  **MODL-CEMT 05-151** Modeling the Influence of Cracking and Healing on Modal Properties of Concrete Beams
Branko Šavija, Delft University of Technology

4:30 pm – 6:30 pm  **Poster Session II – Jr. Ballroom C**
- Bio-Inspired Materials
- Biomaterials
- Coatings & Paints
- Fiber-Reinforced Composites
- Functional Applications
- Materials Characterization
- Mechanochemistry
- Microcapsules: Polymers
- Microvascular Systems
- Supramolecular Polymers
- Thermoplastics & Thermosets
Wednesday, June 24, 2015

7:45 am – 8:00 am  Brief Announcements and Call to Order – Jr. Ballroom B

8:00 am – 9:00 am  Plenary Session V – Jr. Ballroom B
Bioinspired Design of Dynamic and Self-Healing Polymers
Zhibin Guan
University of California, Irvine

9:15 am – 10:30 am  THREE CONCURRENT SESSIONS

Chair: Nele De Belie, Ghent University

9:15 am – 9:30 am  BACT O1-211 Optical Oxygen Sensor Techniques for the Development and Optimization of Bacteria-based Healing Agent for Concrete
Henk Jonkers, Delft University of Technology

9:30 am – 9:45 am  BACT O2-170 Bacteria-based Agent for Self-healing Marine Concrete
Damian Palin, Delft University of Technology

9:45 am – 10:00 am  BACT O3-65 Self-healing of Cracks in Cement-based Materials by Carbonic Anhydrase Microbiologically Precipitation Calcium Carbonate
Chunxiang Qian, Southeast University

10:00 am – 10:15 am  BACT O4-194 Reduction of Water Permeation through Cracks in Mortar by Addition of Bacteria based Healing Agent
Renee M. Mors, Delft University of Technology

10:15 am – 10:30 am  BACT O5-66 Performance Comparison of two Bacteria-based Additives used for Self-healing Concrete
Mian Luo, Southeast University

II. Fiber-Reinforced Composites I – Jr. Ballroom A2
Chair: Veronique Michaud, Ecole Polytechnique Fédérale de Lausanne (EPFL)

9:15 am – 9:30 am  FIBR O1-79 Synthesis of Catalysts Immobilized Carbon Nanomaterials for Self-healing Polymer Composites
Sravendra Rana, Martin-Luther University Halle-Wittenberg
Wednesday, June 24, 2015

9:30 am – 9:45 am  **FIBR 02-225**  Manufacturing of Unidirectional Epoxy-Resin/Thermoplastic-Particle Carbon-Fiber Prepreg for Solvent-Based Self-Healing  
Sang Yup Kim, University of Illinois at Urbana-Champaign

9:45 am – 10:00 am  **FIBR 03-96**  Healing of Early Stage Damage of Ionomer Composite Interlayers by Localized Heating upon Magnetic Induction  
Wouter Post, Technical University of Delft

10:00 am – 10:15 am  **FIBR 04-168**  Evaluation Method of Fracture Properties of Fiber-reinforced Self-healing Ceramics  
Hirotaka Koyanagi, Yokohama National University

10:15 am – 10:30 am  **FIBR 05-219**  Graphene Supported Copper (I) Nanoparticels for Self-healing Nanocomposites  
Ali Shaygan Nia, Martin-Luther University Halle-Wittenberg

**III. Functional Applications I – Jr. Ballroom A3**  
Chair: Jasper Michels, Max Planck Institute for Polymer Research

9:15 am – 9:30 am  **FUNC 01-198**  Improvement of Strain of Vulcanised Isobutylene Isoprene Rubber (IIR) using a Heat Sensitive Ionomeric Mechanism  
Javier Lopez, GKT Gummi und Kunststofftechnik Fürstenwalde GmbH

9:30 am – 9:45 am  **FUNC 02-113**  Stimuli-Responsive Nanocarriers for Self-Healing in Corrosion Protection  
Li-Ping Lv, Max Planck Institute for Polymer Research

9:45 am – 10:00 am  **FUNC 03-86**  Effect of Filler Particle Parameters on Thermal and Mechanical Healing of Thermal Interface Materials  
Nan Zhong, Delft University of Technology

10:00 am – 10:15 am  **FUNC 04-264**  Controlling the Healing Ability of Thermally Reversible Polymer Networks with Light  
Anne Fuhrmann, Humboldt-Universität zu Berlin
Wednesday, June 24, 2015

10:15 am – 10:30 am  **FUNC 05-219** Multicompartment Nanofibers for Stimulus-responsive Self-healing Process  
Shuai Jiang, Max Planck Institute for Polymer Research

11:00 am – 12:15 pm  **THREE CONCURRENT SESSIONS**

**I. Bacteria-based Cementitious Materials II – Jr. Ballroom B**  
Chair: Toshiharu Kishi, The University of Tokyo

11:00 am – 11:15 am  **BACT 06-172** Identification of Concrete-compatible Bacteria and their Application Potential for Self-healing Concrete Products  
Henk M. Jonkers, Delft University of Technology

11:15 am – 11:30 am  **BACT 07-255** Field Application of Self-healing Concrete with Natural Fibres as Linings for Irrigation Canals in Ecuador  
M.G. Sierra-Beltran, Delft University of Technology

11:30 am – 11:45 am  **BACT 08-214** Chloride Transport under Compressive Load in Self-healing Concrete  
Balqis Binti Md Yunus, Delft University of Technology

11:45 am – 12:00 pm  **BACT 09-124** The Feasibility of Encapsulation of Self-healing Bacterium with Ethyl Cellulose  
Bing Liu, Shenzhen University

12:00 pm – 12:15 pm  **BACT 010-221** Mechanical Regain due to Autogenic Healing in Cementitious Materials  
Benoit Hilloulin, Ecole Centrale de Nantes

**II. Fiber-Reinforced Composites II – Jr. Ballroom A2**  
Chair: Mani Diba, Radboud University Medical Center

11:00 am – 11:15 am  **FIBR 06-222** Interfacial Remendability of Glass Fiber-Epoxy Composites Evaluated by Combined Single Fiber Fragmentation and Fatigue Testing  
Giuseppe Palmese, Drexel University
Wednesday, June 24, 2015

11:15 am – 11:30 am  **FIBR 07-193** Assessment of Solvent Capsule-based Healing for Woven E-glass Fibre-reinforced Polymers

11:30 am – 11:45 am  **FIBR 08-233** Microvascular-based Hierarchical System for Sensing-Healing of Delamination in Composite Structures
Shu Minakuchi, The University of Tokyo

11:45 am – 12:00 pm  **FIBR 09-257** Self-healing of Delamination Damage in Vascular Double Cantilever Beam Specimens
Kevin Hart, University of Illinois at Urbana-Champaign

12:00 pm – 12:15 pm  **FIBR 010-40** Towards Self-Healing Composite Structures: Application of Novel in-situ Repair Solutions for Aerospace Structures
Tim Coope, University of Bristol

### III. Functional Applications II – Jr. Ballroom A3
Chair: Michael Dickey, North Carolina State University

11:00 am – 11:15 am  **FUNC 06-244** Self-Healing Si Composite Li-ion Battery Anodes Enabled by Dynamic Ionic Bonding
Sen Kang, University of Illinois at Urbana-Champaign

11:15 am – 11:30 am  **FUNC 07-13** Assisted and Autonomous Repair Strategies in PEDOT: PSS-Based Devices for Printable Organic Electronics Applications
Dr. Jasper J. Michels, Max Planck Institute for Polymer Research

11:30 am – 11:45 am  **FUNC 08-287** Multi-responsive Polymers for Advanced Applications
Darlene K. Taylor, North Carolina Central University

11:45 am – 12:00 pm  **FUNC 09-234** Microcapsule-based Time Release of Battery Additive for Lithium-Ion Batteries
Taewook Lim, University of Illinois at Urbana-Champaign

12:00 pm – 12:15 pm  **FUNC 010-157** Towards the First Developments of Self-Healing Robotics: Thermo-reversible Diels-Alder Polymer Networks in Compliant Actuators.
Seppe Terryn, Vrije Universiteit Brussel (VUB)
Wednesday, June 24, 2015

1:45 pm – 2:45 pm  
Plenary Session VI – Jr. Ballroom B  
Beyond Healing: Autonomous Detection, Protection and Restoration of Damage in Polymers and Composites  
Nancy Sottos  
University of Illinois, Urbana-Champaign

3:00 pm – 4:15 pm  
THREE CONCURRENT SESSIONS

Chair: Henk Jonkers, Delft University of Technology

3:00 pm – 3:15 pm  
BACT O11-263 The Requirements for Autonomic Microbiologically-induced Calcite-precipitation in Concrete  
Kevin Paine, University of Bath

3:15 pm – 3:30 pm  
BACT O12-77 A Three-dimensional Numerical Research on Probability Characteristics of a Crack Hitting Capsules for Self-healing Concrete  
Zichao Pan, Delft University of Technology

3:30 pm – 3:45 pm  
BACT O13-271 A Vascular System for Self-healing Granular Materials  
Abhijit Mukherjee, Curtin University

3:45 pm – 4:00 pm  
BACT O14-106 Preparation of Water-proof and Biocompatible Microcapsule for Self-healing Concrete  
Guangming Zhu, Shenzhen University

4:00 pm – 4:15 pm  
BACT O15-88 Preparation and Optimization of Bio-based and Light Weight Aggregate-based Healing Agent for Application in Concrete  
Eirini Tziviloglou, Delft University of Technology

Chair: William M. Reichert, Duke University

3:00 pm – 3:15 pm  
MVAS O1-277 Development of 3D Printed Vascular Networks for Repeated Healing Cycles  
Isabel Qamar, University of Bristol
**Wednesday, June 24, 2015**

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<tr>
<td>3:15 pm – 3:30 pm</td>
<td><strong>MVAS 02-209</strong> Restoration of Catastrophic Damage in Polymers</td>
<td>Brett P. Krull, University of Illinois at Urbana-Champaign</td>
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<td>3:30 pm – 3:45 pm</td>
<td><strong>MVAS 03-202</strong> Impact Puncture Restoration in Bulk Polymers</td>
<td>Ryan C. R. Gergely, University of Illinois at Urbana-Champaign</td>
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<td>3:45 pm – 4:00 pm</td>
<td><strong>MVAS 04-217</strong> Bioinspired Microvascular Networks for Multifunctional Composites</td>
<td>Jason Patrick, University of Illinois at Urbana-Champaign</td>
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<td>4:00 pm – 4:15 pm</td>
<td><strong>MVAS 05-64</strong> Microvascular Materials for Gas Capture and Self-Improvement</td>
<td>Aaron Palmer Esser-Kahn, University of California, Irvine</td>
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Chair: Patricia Dankers, Eindhoven University of Technology

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<tr>
<td>3:00 pm – 3:15 pm</td>
<td><strong>MODL-POLY 01-89</strong> Mathematical Models of Skin Wound Healing: A Guide in the Development of Synthetic Polymer Coatings</td>
<td>Etelvina Javierre, Centro Universitario de la Defensa</td>
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<td>3:15 pm – 3:30 pm</td>
<td><strong>MODL-POLY 02-188</strong> Modeling the Fracture Behavior of Thermal Barrier Coatings in the Presence of Healing Particles</td>
<td>Jayaprakash Krishnasamy, Delft University of Technology</td>
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<tr>
<td>3:30 pm – 3:45 pm</td>
<td><strong>MODL-POLY 03-300</strong> Welding and Healing of Polymer Interfaces: Connecting Structure, Dynamics and Strength</td>
<td>Ting Ge, University of North Carolina - Chapel Hill</td>
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<tr>
<td>3:45 pm – 4:00 pm</td>
<td><strong>MODL-POLY 04-284</strong> Enhanced Strain Recovery of Polymer-Grafted Nanoparticles Networks by Addition of Biomimetic Catch Bonds</td>
<td>Badel L. Mbanga, University of Pittsburgh</td>
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<td>4:00 pm – 4:15 pm</td>
<td><strong>MODL-POLY 05-183</strong> A Parametric Study of Crack-healing Particle Interaction as a Function of the Mechanical Properties of the Constituent Phases</td>
<td>Sathiskumar A. Ponnusami, Delft University of Technology</td>
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Instructions for Presenters

Oral Session Presenters:

- Upload your talk on the conference computer using a USB flash drive in the speaker ready room several hours before your session is scheduled to begin.
  - Speaker Ready Room – Meeting Room 4
  - Hours:
    - Sunday, June 21 – 6:00 pm – 7:00 pm – for Monday, 6/21 sessions
    - Monday, June 22 – 7:30 am – 5:00 pm - recommend uploading all other sessions
    - Tuesday, June 23 – 7:30 am – 8:00 am, 10:30 am – 11:00 am, 12:15 pm – 1:45 pm
    - Wednesday, June 24 – 7:30 am – 8:00 am
- Click through your uploaded talk to ensure that all of the slides and videos are working and have the desired appearance.
- There will be no live streaming in the session rooms so all videos need to be embedded in your talk.
- If your video is not working for some reason then describe as best you can what people should have seen and keep moving.
- Avoid using distracting and unnecessary slide transitions, graphic features and sounds. Keep it simple.
- Be present in the session room at least 5 minutes before your session begins and take a seat near the front of the room.
- Leave 2 minutes at the end of your 15 talk for questions and do not run your talk to the full 15 minutes. A rough rule of thumb is to have no more than 10 slides in your presentation for a 15 minute talk.

Poster Session Presenters:

- Poster size: 3-ft (92 cm) tall, 4-ft (124 cm) wide. Over-sized posters are discouraged, and there may not be sufficient room to accommodate them.
- The poster title should be well-labeled and legible from a distance of 10-ft (3 m). Letters in the title should be at least 1 inch tall (2.5cm). All lettering should be bold type, use a large font size (24 point font) on a white background. Use 1-inch (2.54 cm) margins. Use upper and lower case letters. Sans serif fonts, such as Veranda, are much easier to read than Serif fonts.
- We can accommodate rolled up posters, folded poster boards, and individually mounted figures and text.
- Mounting clips will be provided to display your posters on the display panels.
- You will be assigned a number for your poster that will be displayed on the display panels (number to be included in your registration packet).
- We suggest you bring business cards to facilitate possible collaborations with viewers.
- No audiovisual equipment will be permitted during the poster sessions.
- Poster Set-Up/Tear-Down Instructions
  - All posters should be set up in Junior Ballroom C by 8:00 am on Monday, June 22. If at all possible, we would like to see all posters on display until June 24. All posters should be removed by 12:30 pm on Wednesday, June 24 for the duration of the conference.
  - Authors need to remain by their posters throughout their assigned poster session: § Session I – Monday, June 22: Cementitious, Ceramics & Metals – 4:30 – 6:30 pm § Session II – Tuesday, June 23: Polymers & Modeling – 4:30 – 6:30 pm

"
Plenary Session 1

Nele De Belie, Ghent University

Self-healing concrete: paving the way for application in practice.

Plenary Session 2

Phil Messersmith, University of California, Berkeley

Molecular Basis of Self-Healing in Wet Biological Adhesives and Their Synthetic Mimics

Plenary Session 3

Rint Sijbesma, Technical University of Eindhoven

Mechanofunctional Polymers: Luminescent Probes and Catalytic Triggers

Plenary Session 4

Jianping Gong, Hokkaido University

Tough and self-healing hydrogels based on reversible sacrificial bonds

Plenary Session 5

Zhibin Guan, University of California, Irvine

Bioinspired Design of Dynamic and Self-Healing Polymers

Plenary Session 6

Nancy Sottos, University of Illinois, Urbana-Champaign

Beyond Healing: Autonomous Detection, Protection and Restoration of Damage in Polymers and Composites
ABSTRACTS

Oral Presentations
BACTERIA-BASED MATERIALS

BACT 01 211 Optical Oxygen Sensor Techniques for the Development and Optimization of Bacteria-based Healing Agent for Concrete
Virginie Witko, t (v.a.witko@gmail.com), Erini Tsiviloglou, Henk M. Jonkers, Technical University Delft, Delft NL

Microbial induced precipitation (MIP), a method by which calcium carbonate precipitation is induced by bacteria, has been proposed as an effective self-healing mechanism in the development of self-healing concrete. The performance of the healing agent is directly linked to the efficiency of the MIP and therefore to the metabolic activity of the bacteria. In order to develop a cost-effective and robust healing agent, its composition should be optimized and fine-tuned to its optimum functionality. This paper presents the use of optical oxygen sensors as a powerful technique for the development and optimization of the bacteria-based self-healing agent developed at TU Delft. The system investigated in this study is based on the metabolic conversion of organic salt through bacterial respiration. The metabolic activity of bacteria exposed to various nutrient sources and the activation time of spores has been monitored with non-invasive oxygen sensors in sealed conditions. Then, the functionality of the bacteria-based healing agent in concrete has been assessed through oxygen profiles measurement with an optical oxygen microsensors. This set up allows the measurement of the oxygen concentration in the water column above the surface of the concrete specimen what can be used to calculate of areal oxygen consumption rates. The results from respiration measurements with the oxygen sensor spots have shown that the bacteria grow best with calcium lactate but interestingly calcium acetate, which is more soluble than calcium lactate, could be also used as an alternative food. The oxygen profile measurement has shown that the healing agent was functional when incorporated into concrete and that the bacteria spores are active after 10h.

BACT 02 170 Bacteria-based Agent for Self-healing Marine Concrete
Damian Palas, Henk Jonkers and Virginie Witko, Technical University Delft, Delft NL

Marine concrete structures are exposed to one of the most hostile of natural environments. Many physical and chemical phenomena are usually interdependent and mutually reinforcing in the deterioration of marine exposed concrete: microcracking due to physical effects increases concrete permeability paving the way for harmful chemical interactions between sea-water, concrete and embedded steel reinforcement. A novel approach to self-healing is a bio-inspired technique, where by bacteria immobilized in concrete are activated through crack induced water ingress, forming a mineral healing precipitate. As a result, cracks are autonomously repaired delaying the ingress of aggressive chemicals. Calcium alginate is presented as a method for encapsulating a specific bio-chemical healing agent for the development self-healing marine concrete. Incorporated in the capsule are bacterial spores and magnesium acetate, latter functioning as a carbon source for the bacteria and acting as a mineral precursor compound required for sealing of cracks. Percentages of alginate to magnesium acetate are optimized to make as much organic carbon available to the bacteria while maintaining capsule integrity. Concrete capsule compatibility is to be tested by the 1% weight addition of the capsules during mixing. Subsequent specimens are to be tested for their compressive strength at 2, 7 and 28 days. While the metabolic activity of the bacteria after encapsulation and mortar inclusion will be conducted through oxygen consumption on split submerged mortar specimens. These results will provide key information for the development of bacteria based self-healing concrete for application in the marine environment.

BACT 03 65 Self-healing of Cracks in Cement-based Materials by Carboxylic Anhydrase Microbiologically Precipitation Calcium Carbonate
Chunxiang Qian, Lifu Ren, Southeast University, Nanjing CN

This research studies the self-healing potential of cracks in cement-based materials incorporating carboxylic anhydrase (CA) bacteria. CA bacteria can accelerate the CO2 hydrated reaction then transfer CO2 to HCO3-. Calcium carbonate deposits when combined with Ca2+. Cement specimens were used throughout the study. Specimens were pre-cracked at the age of 7, 14, 28, 60 days, the width of cracks were between 100 and 1000 μm. Thereafter, the specimens were submerged in water exposed to atmosphere. The experimental results indicated that the CA bacteria showed excellent cracks closing ability to small cracks formed at early age of 7 days, cracks below 400 μm was almost completely closed. The repair effect reduced with the increasing of cracking age. When the bacteria were immobilized by ceramsite, the self-healing effect could be improved for the cracks formed at late ages. Cracks width influenced self-healing effectiveness significantly. Repair ability was restricted when the cracks width were between 500-800 μm and is invalid when the cracks width up to 900 μm. The transportation of CO2 and Ca2+ controlled the self-healing process. It was hypothesized that the diffusion of CO2 and Ca2+ conformed to Fick law in this study. The computer simulation analyses revealed the self-healing process and mechanism of microbiologically precipitation induced by CA bacteria. Moreover, it also explained why cracks closing only occurred on the surface of specimen.

BACT 04 194 Reduction of water permeation through cracks in mortar by addition of bacteria based healing agent
Renée M. Mors, (RM. Mors@tudelft.nl), Henk M. Jonkers, Technical University of Delft, Delft NL

Water tightness in cracks in mortar and concrete constructions requires stringent limitations on crack widths. Practical guidelines for concrete recommend maximum crack widths of 200 μm, based on the autogenous healing capacity of the cementitious material. Here crack paths are mainly blocked by formation of calcium carbonate due to carbonation of portlandite minerals present at the crack surface. Additional production of calcium carbonate may enhance the healing capability, slackening limitations on crack width for regain of water tightness. Carbonates can be formed in the alkaline cementitious environment by bacterial metabolic conversion of a precursor compound. Proposed is the addition to the cementitious mixture of a scalable healing agent, consisting of lactate derivatives as a microbial metabolic carbon source, nutrients for bacterial activation and bacterial spores. Healing agent particles of size 1-4 mm were produced at a 10 kg/h scale. During preparation of the cementitious mixture, particles were mixed in with the sand fraction of the dry constituents. Particles retained integrity during the mixing phase, as intact particles remained visible in the set mortar matrix. Cracked mortar samples and exposed mortar embedded healing agent particles were immersed in water, followed by oxygen measurements for establishing metabolic activity of bacteria. Mineral formation inside cracks of water immersed mortar samples was observed. Regain of functionality in the form of water tightness was indicated by reduction of water permeation through cracks after a healing regime. In this procedure, water permeation of cracked specimens was determined before, during, and after incubation in either water or exposure to 95% relative humidity up to 70 days. Mortar specimens of both control and healing agent containing series featuring crack width below 200 μm appeared completely healed. However, reduction of permeability of specimens with reopened crack widths above 400 μm was found significantly enhanced for healing agent containing specimens.
Concrete as a structural material has received extensive use all over the world. However, cracking in concrete constantly occurs due to its low tensile strength. The presence of cracks may seriously endanger the material durability as cracks allow aggressive agents to penetrate into the concrete matrix. Bacteria-based self-healing concrete as a relatively new technique is important to improve the concrete durability. In the present study, two bacteria-based additives (TYPE 1 and TYPE 2) were respectively used to improve concrete self-healing capacity mainly achieved by bacteria induced mineral precipitations. The crack-healing capacity of cement paste specimens with both bacteria-based additives was evaluated by area repairing rate and water permeability test. Moreover, the mechanical and carbonate resistance properties of cement paste specimens were compared. Experimental results showed that both bacteria-based additives could be used to achieve the goal of concrete crack self-healing. However, the capacity of concrete crack self-healing dropped significantly along with the extension of cracking age. Both bacteria-based additives had little effect on compressive strength and carbonate resistance property. Incorporation of TYPE 1 and TYPE 2 in cement paste resulted in about 6.8% and 2.2% decrease in compressive strength respectively after 7 days curing. The carbonation depths of control specimens, specimens with TYPE 1 and specimens with TYPE 2 were 6.6 mm, 7.0 mm and 6.5 mm respectively after 3 days of accelerated carbonation. We therefore conclude that both additives shows potential for developing self-healing concrete, but the performance of TYPE 2 seems to be better.

Identification of concrete-compatible bacteria and their application potential for self-healing concrete products
Henk M. Jonkers (h.m.jonkers@tudelft.nl) Technology University of Delft, Delft NL

Concrete is presently the most used construction material worldwide. Micro crack formation is a typical concrete-related problem often causing premature material degradation and a reduction in constructions service life. Costly manual maintenance and repair actions are therefore repeatedly needed to combat crack-related problems. This study reports about the isolation procedure of a special group of concrete-compatible bacteria, i.e. bacteria that survive the mixing and hardening process of the concrete mixture. All strains obtained from mineral desert crusts and high pH soda lakes appeared closely related to spore-forming alkaliphilic (alkali tolerant) species (B.cohnii and B.pseudofirmus) of the genus Bacillus. In this study it is furthermore demonstrated experimentally that it is actually the spores but not the vegetative (active) cells which tolerate incorporation in the highly alkaline cement paste and that activation of mortar embedded bacterial spores can mediate the production of calcium carbonate based mineral precipitates resulting in sealing of occurring cracks. The conclusion of this study therefore is that alkali-resistant spore-forming bacteria of the genus Bacillus are required for the preparation of a bacteria-based concrete self-healing agent as non-spore forming species do not survive concrete incorporation. A variety of healing agents based on these bacterial spores are currently being tested in our laboratory, such as lightweight expanded clay particles and Taylor made tablets featuring either an organic- or mineral protective coating. In addition to these latter agents, which are designed for application in either new constructions or self-healing repair mortars, a liquid concrete repair system for treatment of existing damaged constructions has also been developed. As several outdoors and full scale tests appeared successful, large scale production and commercial development of these healing agents is currently being explored.

Field application of self-healing concrete with natural fibres as linings for irrigation canals in Ecuador
M.G. Sierra-Beltran (m.g.sierrabeltran@tudelft.nl), H.M. Jonkers, Technical University of Delft, Delft NL W. Mera-Ortiz, Universidad Catolica de Santiago de Guayaquil EC

This paper describes the first field application of self-healing concrete with alkaliphilic spore-forming bacteria and with Abaca fibres. The application took place in the highlands in Ecuador in 2014. The concrete was cast as linings for an irrigation canal that transports water from glaciers in the Andean mountains to agricultural fields. This canal has been used for over a century by the local farmers. Until not long ago the walls and bottom of the canals were simply made out of compressed soil without any concrete. The yield of the canal was therefore very low: about 70% of the water was lost due to evaporation and infiltration into the soil. In order to improve the functionality of the canal it was then decided to line it with concrete. Unfortunately within one year the concrete cracked so that water was now wasted through the cracks. Self-healing concrete reinforced with natural fibres was proposed as a solution to this problem. The use of fibres in concrete increases the tensile capacity of concrete and assures a controlled crack width. Abaca fibres were selected due to their mechanical properties and availability, as they are a fibre indigenous to Ecuador. Additionally, Abaca fibres have already been studied as reinforcement for mortar to improve the structural behaviour of houses in Ecuador under seismic forces. The bacteria are included in the concrete in order to seal possible cracks. The mechanical properties of the concrete with fibres and bacteria were first evaluated in the laboratory by means of flexural and compression tests. The compressive strength fulfilled the requirements for the intended application in irrigation canals. The self-healing capacity of the concrete with and without bacteria was studied by monitoring the crack-healing. The concrete was designed to favour the use of locally available materials and following mixing procedure that can be replicate by the local communities.

Chloride Transport under Compressive Load in Self-healing Concrete
Balaji Binit, Md Yunus (B.BinitMdYunus@tudelft.nl), Jonkers H.M., Schlangen E. Technical University Delft, Delft NL

A novel experiment was carried out in this study to investigate the effect of compressive load on chloride penetration in self-healing concrete consuming bacterial-based healing agent. Bacteria-based healing agent with the fraction of 2 mm – 4 mm of particles sizes was used in this contribution. ESEM was applied to study samples which were taken by cutting the area of prisms in contact with the chloride solution and together with LIBS method to measure the total chloride content of bacterial concrete. Three load parameters of the compressive load are proposed to describe the phenomena of chloride transportation in bacterial concrete by which the results in prediction analysis of concrete performance within service life were much affected by different percentage of mechanical damage. It was found that the particles sizes of healing agent used leads to more porous-structure of concrete and reduced the strength of bacterial concrete. These affect the transport rate of chloride in concrete. However, in general it is observed that bacteria-based healing agent can still be considered as a measure of protection to concrete under combined action.
BACT 09 124 The feasibility of encapsulation of self-healing bacterium with ethyl cellulose
Bing Liu (jlbingle@szu.edu.cn), Jinlong Zhang, Wenfeng Cheng, Xu Meng, Guangming Zhu, Ning Xu Han, Feng Xing, Shenzhen University, Shenzhen CN

Occurrence of crack inside concrete is one of the inevitable inherent weaknesses of building structures during their service period. The process allows water, salts and chemicals to seep through the cracks, possibly reducing the life of concrete structure. Recently, the application of bacterial-based self-healing technology, which is based on microbial induced calcium carbonate precipitation, has been drawing much attention in the repair of concrete crack. However, due to the high internal pH, relative dryness and the small size of pores inside concrete, it is necessary to set up a protection strategy for self-healing bacteria before their introduction into concrete. In this work, ethyl cellulose (EC), a pH sensitive material, was used to fabricate microcapsule to encapsulate an alkaliphilic spore-forming bacterium. The technical feasibility of encapsulated spores, the influence of pH value and four kinds of organic solvents (methylbenzene, ethanol, acetone and ethyl acetate), which were used for the fabrication of microcapsule, on the calcium precipitation activity (CPA) of the bacterium were studied. In addition, an alkaline pH condition was designed to characterize the releasing performance of the microcapsule under a simulated concrete environment. Further, the CPA of broken/unbroken microcapsules was evaluated, and the micro-morphology of the precipitation produced by the bacterium was investigated through X-ray Diffraction (XRD) and X-ray energy dispersive spectroscopy (EDS). The results showed that compared with unbroken microcapsules, higher CPA was achieved by breaking the microcapsule to release the bacterium, suggesting good protection for the encapsulated spores. Four organic solvents showed harmful influence on the spores, while ethanol was relatively less harmful. Production of calcium carbonate was confirmed by XRD and EDS. Our results also found that releasing of the self healing bacterium from EC microcapsule could be controlled by pH values. With the increase of pH value, the releasing rate decreased greatly.

BACT 010 221 Mechanical regain due to autogenous healing in cementitious materials
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Concrete's intrinsic ability to heal, called autogenic healing, has been reported for many years. This natural process is being improved and supplemented for some years by promising engineered additions such as mineral additions, capsules containing healing agents, minerals producing bacteria, or fibres limiting the crack width. However, a deeper understanding of the natural phenomenon could help to design innovative healing solutions based on cementitious materials themselves. In this study, self-healing potential of cementitious materials is studied both experimentally and numerically, modifying a hydration code (CEMHYD3D) and coupling it with a mechanical code (Cast3M). Experimental work, based on three-points-bending tests, has been conducted on specimens preferentially cracked at early age to investigate their healing potential according to various parameters (e.g. healing time, initial crack width, age at cracking and water-to-cement ratio). A focus is put on the minimum time to obtain mechanical regain for a given crack width in order to explain the development of the healing phenomenon and compare the results with the simulations. Experimentally, small cracks with a width of around 10 μm can quickly heal within several days by immersion into water. Mechanical regain up to 80% of an uncracked specimen is observed for several water-to-cement ratios and is proportional to the initial crack width. The major influencing parameter is the age at cracking; when the crack is created after 72 h, the mechanical regain is considerably decreased and the healing period needs to be several weeks. Numerical models can provide further information. The mechanical regain is due to the formation of bridges between the two cracks lips by ongoing hydration. According to the model, the major healing products in the crack are portlandite and calcium silicate hydrate.

BACT 011 263 The requirements for autonomous microbiologically-induced calcite-precipitation in concrete
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Self-healing of concrete using microbiologically-induced calcite-precipitation is complex as it is necessary to encapsulate the ingredients (bacteria, nutrients and organic precursors) within the concrete during the mixing stage and maintain them within an inert condition until such time that a crack appears and healing is necessary. Consequently it is necessary that any ingredient used does not affect the setting and hardening of the concrete. Once a crack appears the ingredients must become active and form calcite rapidly within the crack without adversely affecting undamaged concrete and steel reinforcement. This restricts the choice of ingredients that may be used. This paper, drawing upon research carried out within the UK Government and industry funded research project, MLA: Materials for Life, addresses this complex problem and describes the requirements for the bacteria, minerals and nutrients to provide autonomous self-healing within concrete. The paper discusses the need to use copious spore-forming alkaliphilic bacteria that germinate relatively quickly and considers the kinetics of microbiologically-induced calcite-precipitation. Issues relating to temperature, pH and health and safety are also discussed. The paper also considers the compatibility of the nutrients and organic precursors with concrete. It is concluded that whilst the encapsulation of bacteria, nutrients and organic precursors that lead to microbiologically-induced calcite-precipitation is readily achievable; optimisation of the process to achieve an economic solution requires further biological and engineering research.

BACT 012 77 A three-dimensional numerical research on probability characteristics of a crack hitting capsules for self-healing concrete
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In self-healing concrete, healing agents (including the bacteria and nutrients for the bacteria) are often sealed in capsules to survive from the mixing of concrete. When the crack occurs, these capsules can be damaged, the healing agents can be released and the chemical actions can be activated. This research mainly focuses on the probability characteristics of a crack hitting the capsules. To conduct the research, the meso-scale models for two kinds of capsules, i.e., spherical and tubular capsules, are established. Statistical analysis is conducted to estimate the hitting probability and the number of capsules damaged by a crack based on the meso-scale models. With the numerical method proposed in this research, it is possible to estimate the efficiency of the self-healing system, as well as optimize the proper usage of the capsules. An application of this numerical method in a bacterial self-healing concrete based on Liapor (a kind of light weight aggregate) is also included.
BACT 013 271 A Vascular System for Self-healing Granular Materials
Abhijit Mulherjee (abhijit.mulherjee@curtin.edu.au), Navdeep Kaur Dhani, Curtin University, Perth AU

During the last hundred years, roads, bridges, railways and buildings are being built at a great pace. As a consequence, monitoring and maintenance of this civil infrastructure and managing the greenhouse gas emission from construction are the two great challenges facing the civil engineering community. Nature achieves self-healing with minimal energy consumption. Microbiologically induced calcite precipitation (MICP) in building materials that harnesses the ability of microbes for generation of carbonates is a promising way of emulating Nature. MICP scores high on sustainability as it happens at ambient conditions and thus, greatly reduces energy consumption and emission of greenhouse gases. The process requires uricolytic bacteria, urea, calcium source and nutrients. Bacteria hydrolyse urea to form ammonia and bicarbonate, which in presence of calcium ions and alkaline pH precipitate as calcium carbonate. Bacteria can deposit carbonates autogenously within the pores or cracks of the substrate materials. Thus, it can be argued that MICP can lead to self-healing if the calcite precipitating bacteria along with a calcium source is present at the site of healing. Prior research has attempted self-healing by both chemical and biological routes. Capsules of the healing fluid have been dispersed in concrete at the time of mixing. In the event of concrete cracking the fluid is released and the crack is healed. We present a vascular system for healing that is also able to monitor the rate of healing. In this system, quite like the cardio-vascular system, the healing fluid is carried into the material through small vessels. The fluid trickles through the material and the effluent is collected through the collecting vessels. By chemically analysing the effluent we monitor the MICP inside the material. In this paper, we illustrate the vascular system and report the indicators in the effluent that manifest the occurrence and rate of MICP.

BACT 014 106 Preparation of water-proof and biocompatible microcapsule for self-healing concrete
Guangming Zhu (gzhu@szu.edu.cn), Yuanchun Luo, Jiaoning Tang, Ningwu Han, Feng Xing, Shenzhen University, Shenzhen CN

In recent years, some bacillus spores were employed as efficient self-healing agents in concrete as these bacteria can biologically induce precipitation of calcium carbonate. Usually, these spores are easy to germinate in the appearance of water, so microencapsulation by a water-proof and biocompatible material is necessary to help them pass the incubation period, especially in the cement-hydration stage. In this paper, Koch's bacillus DSM6307 was microencapsulated by hydrophilic epoxy resin in polymethylsiloxane sol-gel. The whole process was conducted in a nonaqueous liquid at low temperature less than 50°C, to avoid the germination or inactivation of spores. Before microencapsulation, the shell materials, epoxy resin and its curing agent, N-(aminomethyl)amino-ethyl trimethoxy silane (silane coupling agent KH792), were mixed together with the core materials, which is consist of spores, cainine, food, avicel carrier, and so on, and then granulated. The formation of microcapsule actually is a curing reaction of epoxy resin with KH792, just by dripping the pills into polymethylsiloxane medium. Polymethylsiloxane was selected because its specific gravity (0.97g/cm3 at 25°C) is similar to that of core materials, so that the pills can be suspended in the reaction medium for a long time. The spores were confirmed to have a chemical tolerance with all the chemicals used in this process. After microencapsulation, the fraction surviving of spores is higher than 90%, indicating the process is bio-friendly. Water-permeability testing shows, there are no microcapsule swollen, and no microencapsulated spore germinated after the obtained microcapsule soaked in water over 10 days.*

BACT 015 88 Preparation and optimization of bio-based and light weight aggregate-based healing agent for application in concrete
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The innovative technology of self-healing concrete allows the material to repair the open micro-cracks that can endanger the structure's durability, due to ingress of aggressive gases and liquids. These harmful substances reach the steel reinforcement easily through open cracks resulting in rapid degradation in time. Various concepts of self-healing concrete use encapsulation techniques, in order to immobilize and protect the required healing agent during mixing and setting. In this paper the bio-based healing agent, consisting of alkaliphilic bacterial spores and organic mineral compounds (feed), is encapsulated into light weight aggregates (LWA). Although, the concept of shielding the healing agent in LWA capsules is simple and effective, there are some challenges regarding the impregnation procedure. In this study a method for efficient incorporation of healing agent into the LWA is developed. Different healing agent solutions (with high and low content of feed), impregnation techniques (with and without vacuum application), and drying conditions (at different temperatures) are examined. The selection of the appropriate procedure is based on the mass increase criterion, supported by light microscope pictures of impregnated particles. The functionality (activation of bacteria) of the selected healing agent-containing aggregates is also validated by oxygen concentration measurements reflecting bacterial metabolic activity. The results obtained in the current study show that the optimized method enhances considerably (approximately 2.5 times) the amount, and therefore efficiency, of healing agent embedded into LWA, in comparison to what was achieved in previous studies. As a consequence, the LWA that are treated with the new incorporation procedure are likely to seal more efficiently occurring cracks and provide better durability protection to concrete.

BIO-Inspired MATERIALS

BIOI 017 273 Bio-inspired metal-coordination: Using more of nature's tricks to assemble biomaterials with multifunctional properties
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A variety of dynamic bonds have been employed as reversible crosslinks in polymer materials in efforts to obtain desirable properties such as stimuli-response, self-healing and shape-memory. Many dynamic bonds utilized so far however, have poor compatibility with aqueous solvents, thereby limiting their use in polymer materials intended for environmental and medical applications. Inspired by marine biological materials, we have been exploring metal-coordinate dynamic crosslinks that allow unique control over metal-binding polymer network properties in aqueous conditions. These early bio-mimetic explorations revealed that certain metal-ligand coordination complexes allow aqueous polymer solutions to be finely tuned between fluids and strong viscoelastic gels, simply by the choice of the coordinating metal ion. Complex hydrgels with multiple mechanical relaxation times can now easily be established by incorporating multiple metal-ions into the same metal-coordinate polymer network. More recently we have begun exploring stimuli-responsive properties of metal-coordinate polymer networks and have found that temperature, pH, magnetic and mechanical stimuli all can induce strong responses in metal-ligand coordinate crosslink dynamics. These demonstrations open the door to design of multi-stimuli-response controlled polymer bio-materials. Early lessons from this pursuit will be presented.
One outstanding phenomena in nature is the recovery of the original state after a damage occurred. This effect could also be found for mussel byssus threads. In that special case different interactions lead to the healing of a mechanical damage. These interactions are mostly metal-ligand interactions, e.g., iron-dopamine. Beside the iron-dopa interaction there is also the zinc-histidine system, which is responsible for the self-healing process. The reversible bonding and debonding of the metal complex result in the recovery of macroscopic properties. In order to understand the mussel system in more detail we transfer this interaction to synthetic polymers. For this purpose, histidine-containing monomers were prepared and copolymerized with different commercially available comonomers by reversible addition chain-transfer (RAFT) polymerization. The resulting polymers were crosslinked by the addition of different zinc salts in order to mimic the natural system. These systems show self-healing behavior at 50 °C. The effect of the counter ion was studied and it could be shown that the non-coordinating nitrates leads to the best self-healing polymers. With this study the first step towards the understanding of the self-healing behavior of mussel byssus threads is done. The transfer of the natural system into synthetic polymers was successful and leads to a better understanding of the molecular structures.

BIOI 03 102 Effect of different curing agents on the fracture behavior of epoxy-shelled bio-microcapsule under stress
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Besides natural biopolymers, such as alginate, chitin, cellulose, gelatin, etc, epoxy also can be a candidate of shell-materials in microencapsulation of bacteria, because epoxy and its amine curing agents, such as N-(amino-ethyl)-amino-propyl triethoxy silane (silane coupling agent KH792), M-Xylene Diamine(MXDA), 2,4,6-Tris(dimethylaminoethyl) phenol (DMP-30), are proved harmless to their spores. Epoxy shell admittedly is superior in waterproofing quality, which is very important to the dormancy of spores, but sometimes it is too strong to be broken. In this work, epoxy shell was crosslinked with E51-shelled microcapsules with KH792, MXDA, DMP-30 were used respectively, and their fracture behavior was examined and compared. It’s found microcapsule with E51/KH792 shell is hard to break up, meanwhile, that with E51/MXDA and E51/DMP-30 shell are more easy. Nano indenter measurement shows, E51/KH792 shell is very tenacious, and E51/DMP-30 shell is brittle. It can be concluded that fracture behavior of microcapsules depends on the molecular chain flexibility of curing agents and the degree of crosslinking of cured epoxy. The molecular of amine curing agent with a long flexible chain or less reactive group will lead to an elastic shell, otherwise, to a fragile shell.

BIOI 04 251 Bio-Inspired stimuli responsive reversible actuation for selective growth
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In biologically engineered architectures, ‘morphogenesis’, a dual strategy for growth and form, exists where: (a) the mechanics of design using morphological constraints involves a practice of dynamic and continuous negotiation between design intent and material emergence; and (b) the proposed biologically produced architecture will behave as an adaptive organism. These materials themselves are capable of self-repair for longevity, self-replication for reproduction, and growing new structures. For example, the Phragmatopoma californica (Sandcastle worm) builds protective structures by joining sand grains together with secreted cement. The cement reacts upon excretion with magnesium and calcium cations using phosphoseresins, a post-translationally modified serine amino acid. This cement has been used as the inspiration for a synthetic hydrogel possessing polychelating properties which uses phosphate functional groups to bind metal cations forming crosslinks between multiple chains, vastly increasing the stiffness and decreasing the swelling potential of the hydrogel. Hydrogels were synthesised from monomers hydroxyethyl acrylate (HEA, 79.25%mol) and ethylene glycol methacrylate phosphate (EGMP, 19.25%mol) and lightly crosslinked with N,N'-methylenebisacrylamide (MBAA, 0.5%mol). Initially the hydrogels were tested for differential swelling in varies solvents, metal cations and pH. The hydrogel showed a positive linear relationship between polar indexes of a variety water miscible solvent and both swelling ratio and volume ratio. All metal cations tested (vanadium(III) and (IV), iron(III), manganese(II) and calcium(II)) caused decreased swelling ability and therefore increased crosslinking. These results and ionoprinting have been used to create hydrogels with stimuli responsive reversible actuation, i.e. transforming flat cruciform shapes into their 3D assembled regular polygons. This technique has also been used to inhibit growth of the hydrogel in selective regions to allow for selective growth.

BIOMATERIALS

BIOM 01 272 Targeting Failure Mechanisms with Self-healing Strategies
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Mechanical failure resistance is an essential requirement of a biomaterial’s biocompatibility; if a biomaterial loses its mechanical integrity, it will no longer function as intended. Different biomaterials manifest different energy absorption mechanisms to resist damage accumulation and eventual catastrophic failure. Broadly speaking, these mechanisms include crazing (polymers), microcracking (ceramics), and plastic deformation (metals); however, a material’s microstructure can produce multiple potential, material-specific, energy absorption mechanisms (e.g., crack diversion), and a material can be engineered to include different failure resistance mechanisms – e.g., the interface between components in composite materials can be optimized to resist fracture. Those mechanisms, combined with the loading environment, will dictate how cracks are generated, move though a material, and ultimately result in material failure. This presentation will discuss how microstructural and composite elements control energy absorption, and hence damage/crack evolution, in different biomaterials, and examine how self-healing strategies can be implemented based on that knowledge. A classical biomaterials example of a multiple component material is poly(methyl methacrylate) bone cement. Bone cement’s microstructure consists of four distinct phases, each contributing differently to crack growth and material failure. This presentation will discuss the details of bone cement fracture, and how understanding the energy absorbing mechanisms can be generalized to different biomaterials. We will examine how additional energy absorbing mechanisms can be incorporated into a material like bone cement. These mechanisms can include changing the microstructure and adding microstructural elements; either can incorporate self-healing components. However, potential energy absorbing systems must address the failure modes of a material - that is, they cannot be such that they are simply ignored and circumvented by a crack, for example. Based on knowledge of the fundamental materials system, we will then explore how self-healing strategies can be used to further enhance performance, prevent or reverse damage and fracture, and increase a material’s biocompatibility.
Dental composites are becoming increasingly popular due to their tooth-like color and appearance. Most short-term failures of dental composites are due to mechanical damage, such as cracking. Therefore, many of these failures might be prevented through the use of a self-healing dental composite. High-quality characterization is critical in the development of self-healing materials. Here we present the fracture testing results of a self-healing dental composite using a new compact tapered double-cantilevered beam specimen (CTDCB). The CTDCB specimen uses approximately six times less material than a traditional TDCB specimen. Development of the CTDCB sample and the fracture behavior of this specimen under quasi-static and fatigue will be discussed. The synthesis and compounding of an initial microcapsule-based self-healing restorative resin will be described and results from fracture-based characterization of the self-healing material will be presented.

**BIOM 03 267 Soft, Stretchable, and Self-healing Liquid Metals**

Michael Dickey (mddickey@ncsu.edu), North Carolina State University, NC USA.

This talk will discuss the properties and applications of a micromoldable liquid metal that can be patterned and embedded in functional polymers to create conductors that are soft, self-healing, conformal, and ultra-stretchable. The metal is a gallium-based metal alloy that is a low-viscosity liquid at room temperature with low toxicity and negligible volatility. Despite the large surface tension of the metal, it can be molded and 3D printed into non-spherical shapes due to the presence of an ultra-thin oxide skin that forms on its surface. The metal can be patterned by injection into microchannels and microvasculature or by direct-write techniques including 3D printing. Because it is a liquid, the metal is extremely soft and flows in response to stress to retain electrical continuity under extreme deformation. By embedding the metal into elastomeric or hydrogel substrates, it is possible to form soft electrodes and optical components, stretchable antennas, and ultra-stretchable wires that maintain metallic conductivity up to ~800% strain. Because it is a liquid, it is also possible to form reconfigurable circuits that can ‘heal’ by forming new shapes in response to pressure or voltage.

**BIOM 04 7 Catalyst-free self-healing bone cement**

Monty Reichert (reichert@duke.edu), Alice Brochu,, Orien Matthys, Vibhav Agarwal, Duke University, NC USA.

The tissue adhesive 2-octyl cyanoacrylate (OCA) was encapsulated in polyurethane microshells and incorporated into bone cement to form a catalyst free, self-healing bone cement comprised of all clinically approved components. The bending strength, modulus, and fatigue lifetime were investigated in accordance with ASTM and ISO standards for the testing of PMMA bone cement. The bending strength of bone cement specimens decreased with increasing wt% contents of OCA without or with OCA, with specimens of <5 wt% capsule content showing minimal effect. In contrast, bone cement bending moduli was insensitive to capsule content. Load controlled fatigue testing was performed in air at room temperature on capsule free bone cement (0 wt%), bone cement with 5 wt% OCA-free capsules (5 wt% No OCA), and 5 wt% OCA-containing capsules (5 wt% OCA). Specimens were tested at a frequency of 5 Hz at a maximum stresses of 90%, 80%, 70% and 50% of each specimen’s bending strength until failure. The 5 wt% OCA exhibited significant self-healing at 70% and 50% of its reference strength (p < 0.05). Fatigue testing of all three specimen types in air at 22 MPa (50% of reference strength of the 5 wt% OCA specimens) showed that the cycles to failure of OCA-containing specimens was increased by two-fold compared to the OCA-free and capsule-free specimens. This study represents the first demonstration of dynamic, catalyst-free self-healing in a biomaterial formulation.

**BIOM 05 48 Self-healing chemistry and electronic applications**

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We recently demonstrated new concepts of applying self-healing chemistry to electronic skin to enable autonomous self-repair of electrodes and sensors. We applied this concept to enable longer operation lifetime of Silicon anodes for lithium ion battery. In addition, we developed new chemistry to enable rapid self-healing, healing under humid conditions or in aqueous conditions, and elastic self-healing materials.

**BIOM 06 204 Regulation of self-healing hydrogels for sequential cell attachment and detachment**

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The ability to regulate the interactions between biomaterials and cells is important for tissue engineering, regenerative medicine and biosensing applications. Traditional methods for the regulation rely on physical stimuli (e.g., light) or enzymes that can induce the structural and functional changes of biomaterials. However, once biomaterials change, it is difficult for the biomaterials to heal. We recently developed a novel hydrogel whose cell binding functionality can be programmed. As a result, the hydrogel can be self-healed in the presence of triggering molecules. This hydrogel was synthesized using oligonucleotide aptamers. Without the triggering stimulation, the hydrogel existed in an inert state; with the triggering stimulation, the hydrogel was activated for cell attachment. The active hydrogel could be stimulated to recover its original inert state that led to cell detachment. More importantly, this self-healing procedure can be repeated for multiple cycles.
BIOM 07 115 A Novel Wound Dressing Based on Ag/Zwitterionic Polymer Hydrogel
Amin GhashamiNejad (ghavaminejad@ibnu.ac.kr), Melisa SamariKhahaj, Ludwig Erik Aguilar, Chan Hee Park, Cheol Sang Kim, Chonbuk National University, KR

Hydrogels are water-swollen polymer networks of interest to the biomaterials community for potential use in a diverse range of applications. There are a few reports on the formation of silver nanoparticles within the polymeric matrix, the developed hydrogels are in the form of bulk hydrogel and, additionally, the embedded metallic nanoparticles can easily escape from the 3D polymeric matrix for antibacterial applications. Herein, zwitterionic hydrogels functionalized with silver nanoparticles were prepared by making use of catechol redox chemistry. For this purpose catechol groups were introdced in the poly-meric network during the cross-linking polymerization process. These groups act as reducing agents of silver ions, which enables the functionalization of the polymeric gel with silver nanoparticles. The novel zwitterionic nanocomposite hydrogel possesses unique features, including 1. biocompatibility; 2. high water content; 3. anti-biofouling properties; 4. strong durability; 5. suppression of bacterial growth; 6. controlled release of Ag ions. Meanwhile, they exhibit excellent biocompatibility, high swelling ratio, and good extensibility. More importantly, in vivo experiments indicate these novel hydrogels can significantly accelerate the healing rate of artificial wounds in rats during 15 day of healing of injured wounds. In the future it may be possible to exploit Ag hydrogels as tissue adhesives or sealants, since the adhesive properties of catechols found in native mussel adhesive proteins and synthetic polymers are well documented. In some surgical situations it may be advantageous for an antibacterial hydrogel to be inherently an antibiotic, for example in the case of external wound repair, surgery of the gastrointestinal tract, or even as a prophylactic measure in general surgical procedures involving adhe-sives and sealants. While further work will be needed to evaluate the efficacy of Ag hydrogels for these applications, we believe these hydrogels have the potential to reduce infection rates in applications where tissue sealants are needed or where biomaterial coatings could be employed.

BIOM 08 289 Supramolecular transient networks in water: from hydrogels to biomedical applications
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Regenerative medicine is an emerging field in which tissues are being stimulated to regenerate by a combination of materials, cells and bioactive factors. The materials used can be of natural or synthetic origin. We propose that synthetic materials are preferred over natural systems because of less batch-to-batch variability, and because of the ability to control the components. Important is that these synthetic materials have the same ability to adapt to natural tissues and cells as natural materials have. There is a need for the introduction of dynamic reciprocity when developing new supramolecular assemblies for regenerative medicine. These biomaterials have to adapt to changes in the regenerating tissue in time and space, and tissues will respond to the biomaterials in a spatiotemporal way as well. Therefore, we aim at the development of biomaterials that are indistinguishable from their natural counterparts. Supramolecular systems based on molecular assemblies are proposed to be eminently suitable for this. Here we report on a modular supramolecular hydrogel system based on the four-fold hydrogen bonding ureido-pyrimidinone (UPy) moiety coupled to various poly or oligo(ethylene glycols). The UPy-modified polymers form supramolecular transient networks in water, and show self-healing behavior depending on their chemical structure. Mixing-and-matching of these UPy-hydrogels yields materials with unexpected and unprecedented properties. Furthermore, this modular supramolecular hydrogel system becomes due to its nonlinear structure and dynamic structure, a vehicle for drug delivery in vivo, or as a possible mimicking of the extracellular matrix in vitro via introduction of bioactivity.

CEMENTITIOUS MATERIALS

CEMT 01 177 Effect of carbonation on autogenous self-healing in cementitious materials
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It has been reported that autogenous self-healing in cementitious materials can only take place when water is present in cracks. When cracks in concrete are filled with water, CO2 from the atmosphere dissolves into the water and diffuses into cracks. CO32- ions slowly diffuse into the crack very slowly through the crack mouth. In this case, reaction products of further hydration of unhydrated cement can be formed in cracks firstly. Meanwhile, portlandite can be recrystallized in cracks after leaching from the bulk paste. As CO32- ions diffuse into the crack gradually, or when the cracks become dry and exposed to atmosphere directly, the newly formed reaction products in the cracks will be carbonated. However, the effect of carbonation process on the effect of autogenous self-healing of cracks is still not clear yet. In this study, the effect of carbonation on self-healing was investigated by thermodynamic modeling. By using thermodynamic modeling, the transformation of phases and the corresponding volume change due to carbonation can be determined. It was found that in the cracks in Portland cement paste, the portlandite formed in the healing process is first transformed into calcite, followed by the carbonation of C-S-H forming calcite and silica gel. Because the carbonation of portlandite increases its volume, the filling fraction of cracks in Portland cement paste is improved by carbonation. In slag cement paste, carbonation of reaction products formed in cracks has a positive effect on the filling of cracks in the beginning of carbonation processes, but has negative effects later on. The change of the filling fraction of crack caused by carbonation depends on the mineralogy of the solids that had formed in cracks before the carbonation process.

CEMT 02 75 Elucidation of Rapid Reduction Mechanism of Water Flow through Concrete Crack Regarded as Self-healing Phenomenon
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The development of self-healing concrete has witnessed several strides in the last three decades. Among these is the understanding of the mechanisms of self-healing concrete, as well as the realization of new technologies of enhancing crack self-healing in concrete. Previous research suggests that crack closing mechanism occurs due to mainly 1) Hydration of anhydrous cement, 2) Formation and crystallization of Calcium Carbonate, 3) Swelling of cement matrix and 4) Sedimentation of particle in the crack interstices. In this research however, after a one by one investigation, it was found that these mechanisms do not fully explain the drastic water flow recovery that occurs in the initial stages of water permeation through cracked concrete. This preliminary finding then prompted direct visual observation of water flow through the narrow crack space. This was achieved by using acrylic resin and glass as transparent media over the concrete surface of split and machine cut cracks respectively. With this, an interesting observation was made, the creation of air bubbles (waterless spaces inside the interstices) following the condition of full water saturation. It was observed that water flow through the narrow crack openings creates air bubbles by probably various water action mechanisms. The created air bubbles narrow water flow paths in the crack, causing significant water flow reduction in the initial and later stages of water supply condition.
Effects of GGBS Content on Self-Healing of Engineered Cementitious Composites
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Slag, the by-product from blast furnace, is often used to partially replace the cement in engineered cementitious composites (ECC), a novel type of fiber-reinforced concrete with self-healing potential. This paper investigated the effects of slag content on self-healing performance of ECC. Three levels of cement replacement ratio up to 60% were studied and the self-healing performance was quantitatively determined through crack width reduction and resonant frequency recovery. The results show that slag content has great influence on the self-healing performance. The addition of GGBS up to 35% enables healing of larger crack (90 micron meter). Optimum slag content, smaller crack width, and water/dry conditioning favor self-healing in ECC.

Effect of fly ash type on mechanical and self-healing behavior of Engineered Cementitious Composite (ECC)
Shunzhi Qian (SZQian@ntu.edu.sg), Nanyang Technological University, SG

This paper aims to clarify the influence of different type fly ash on the mechanical and self-healing behavior of Engineered Cementitious Composite (ECC). Five different types of fly ash, which has different chemical and physical properties, were used in ECC mixture with a fly ash to cement ration of 2.2. The compressive and uniaxial tensile tests were conducted to evaluate the influence of fly ash type on mechanical properties, including compressive strength, tensile strain capacity and crack patterns of ECC specimens at the ages of 7, 28 and 90 days, respectively. The rapid penetration test was used to assess effect of fly ash type on self-healing behavior of ECC. Chemical characteristics of the self-healing product of different ECC specimens were examined by environment scanning electron microscope (ESEM) and energy dispersive X-ray spectroscopy (EDS). The hydration heat of different fly ash was investigated to clarify the influence of fly ash type on ECC mechanical and self-healing properties. The fly ash with lower reactivity composition (SiO2, Al2O3 and Fe2O3) has a positive influence on tensile strain capacity, but with a reduced compressive strength at early age. The lower reactivity ash result in larger crack width at the same pre-damage level, which leads to a slower self-healing process. The self-healing product is a mixed C-S-H/CaCO3 system with the CaCO3 as the main ingredient, therefore the fly ash with a high CaO is beneficial for self-healing of ECC.

Self-Healing of High-Performance Fibre-Reinforced Cementitious Composites
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Cracks have many negative effects on the durability and mechanical properties of concrete. Preventing cracks is important especially for watertight structures for the prolonging service life. Self-healing of high performance fiber reinforced concrete was investigated in this study. For this purpose, two concrete mixtures were designed for the production of the textile reinforced concrete specimens. Binder in the first mixture was CEM I and in the second mixture they were CEM III, fly ash and silica fume. Super absorbent polymers (SAPs) were added to the first composition as a third constituent in order to observe their effects on self-healing. Specimens were cast as rectangular prisms. After demoulding they were wrapped in plastic foil and kept in climate room for 28 days. The tensile test was chosen for the controlled pre-cracking, the rate of displacement was 3mm/min. After pre-cracking, specimens were exposed to different curing conditions during 2 and 4 weeks. Specimens were exposed to air, water, wet-dry cycle I (water-1h, lab. climate-23hrs) and wet-dry cycle II (water-1h, lab. climate-7hrs) to simulate outdoor environment. Uniaxial tensile test, optical microscope analysis, thin sections analysis, scanning electron microscopy, EDX analysis and MIP tests were performed. It can be concluded that self-healing products, which were attached to the cracks, are leading to recovery of mechanical performance. Air curing showed no self-healing in all groups. Longer water curing and wet-dry cycling are increasing mechanical healing performance. Specimens that were produced with CEM I and cured for longer time showed the best self-healing behavior because of unhydrated cement left. Addition of SAP materials supported further hydration and affected mechanical properties positively for less time wet-dry cycle. Presence of water in cracks is the most important factor for self-healing. However, the healing capacity for CEM I was the highest. Newly formed self-healing products in the cracks were mostly combination of C-S-H phases and calcites. Specimens which exposure to wet-dry cycling were denser structures than air cured specimens in MIP tests.

Sodium silicate particles encapsulated in epoxy resin for self-healing cement-based materials
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Preparation process of a new healing agent for cement-based materials is revealed in this paper. The healing agent is made of sodium silicate particles, which are encapsulated in epoxy resin. Fine sands are further coated on the epoxy resin surface in order to facilitate the rupture of healing agent. Healing agents of irregular shapes are obtained by adopting specific procedures, and incorporated into Strain Hardening Cementitious Composite (SHCC). SHCC specimens at the age of 28 days are cracked by 4 point-bending tests followed by wet curing for 3 days. Crack filling behaviour and micro-mechanical property of healing products are studied by means of Scanning Electron Microscope (SEM), Energy Dispersive Spectrometer (EDS) and Nano-indentation, etc. Healing efficiency is evaluated by ultrasonic velocity measurements and 4-point bending tests. The results show that after wet curing, healing product mainly composed of calcium silicate hydrate is formed in the cracks of cement-based material. Elastic modulus of healing product measured by nano-indentation is comparable to the one of C-S-H gel from the cement-based matrix. Furthermore, the amount of healing product is much larger compared to the one found in reference samples where only autogenous self-healing takes place. Healing agent particles of the size from 2 to 4 micrometres are chosen to optimise the volume fraction to be incorporated in SHCC. Some improvement on the ductility of SHCC is observed when a proper volume fraction of healing agent is incorporated. It is concluded that the proposed healing agent shows a good potential for the self-healing of cement-based materials.
This paper studies the potential of using magnesium oxide (MgO) based pellets to improve the crack self-healing capability of concrete. Two types of pellets with (1-2) mm diameter were utilized in this study. The first was developed in the laboratory from expansive minerals such as reactive MgO and Bentonite and the other type is a commercial MgO pellets. Both types were coated of polyvinyl alcohol (PVA) film layer to sequester the core materials until the crack time. The coated pellets were replaced the fine lightweight aggregates by 10% in mortar concrete samples. The self-healing efficiency was verified through different tests e.g. three point flexural strength and monitoring cracks closure using optical microscope images. It was shown that the addition of 10% of the both types of pellets increases the compressive strengths at 7, 28, and 56 days. Furthermore, the coated fabricated pellets and the commercial ones presented ~35% and 8% strength recovery respectively, in contrast to the reference samples which showed less than 2% strength recovery at the same age. The microscopic investigation showed complete cracks closure for concrete samples contained any of the two coated pellets types. Overall, the fabricated MgO/ Bentonite pellets showed promising results in both crack sealing and strength regain compared to the reference samples and those contained the commercial MgO pellets.

CEMT 08 256 Cementitious materials with mineral additions : impact on the self-healing kinetics and the products formation
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Ground granulated blast-furnace slags (GGBFS), as a hydraulic binder, are widely used for many years in engineering concretes. The French standards allow substituting 50% of Portland cement by GGBFS. This approach leads to a decrease in the CO2 emissions produced during clinkerisation process. Portland cement substitution by GGBFS can also improves the workability, decreases the hydration heat and increases the long-term compressive strength. GGBFS can also significantly improve the resistance to sulfate attack. Concrete structures made with GGBFS cement can be cracked at early age due to restrained shrinkage. This cracking can reduce mechanical and transport properties, leading to an increased risk of aggressive agents penetration. Self-healing of cracks, already observed on building sites, could partially overcome these durability issues. To understand the effect of GGBFS on self-healing kinetics and the type of self-healing products, five hydraulic binders were studied: two Portland cement (French and Canadian), two GGBFS (French and Canadian) mixed with Portland cement (named GGBFS formulation hereafter) and a French blended cement (62% of slag) named CEMIII/A. Each material was characterized by XRF, XRD, PZD test, fineness Blaine test and TGA. At 7 and 28 days, French and Canadian mortar specimens were cracked respectively to obtain three crack sizes : 50, 100 and 150 µm. The cracked specimens were then stored at 23 °C and 100% R.H for up to 6 months. The evolution of self-healing is followed by X-ray tomography or air-flow measurements. SEM with EDS was performed on the sawed samples to identify and analyze self-healing products. Results show that two main products are formed: (1) calcite by the carbonation of portlandite in the matrix, and (2) supplementary reaction products (mainly C-S-H with various C/S ratios), formed by the reaction of anhydrous particles. Both GGBFS formulations show a good self-healing potential but the kinetics of the phenomenon are slightly different. Mortar made with French GGBFS presents the best self-healing potential compared to the four others formulations. Mortar with Canadian GGBFS presents a similar behavior as Canadian Portland cement. These results can be explained by the material characteristics but also by their hydration kinetics. A hydration model is currently developed in order to investigate more deeply these observations.

CEMT 09 73 Influence of expansive minerals on the self-healing of cement paste and mortar systems
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Expansive minerals have great prospects for improving the self-healing capacity of concrete. Once a crack starts to propagate in concrete, an incorporated expansive mineral could hydrate and expand hence bridging and healing the cracks. This study investigates the improvement of the self-healing capacity of Portland Cement (PC) based cement paste and mortar system using MgO, bentonite clay and quicklime minerals. Optimum mix proportions for improving the autogeneous self-healing capacity of PC were investigated first. Mechanical strength development and chemical properties were investigated for different mix proportions and self-healing capacity was compared using crack sealing percentage, and flexural strength recovery in 28 days. In the second stage, different minerals including the optimum self-healing cement mix were encapsulated within glass capsules then embedded into the mortar prisms for investigating self-healing capacity. Self-healing efficiency of capsule containing mortar specimen were investigated in three different curing conditions (ambient, high humidity, and immersed in water). Similar self-healing evaluation method was adopted as it was for evaluating self-healing efficiency for the cement paste. Further microstructural investigation was carried out on self-healing materials for characterising self-healing compounds using FT-IR, XRD, and SEM. Promising self-healing performance was found with expansive minerals in immersed condition, although limited healing happens in high humidity condition and least self-healing was observed in specimens stored in ambient condition. In immersed healing state, several cracks up to 500 µm had effectively sealed within 7 days in the sample containing optimum self-healing cement mix. However, liquid mineral containing samples had sealed considerably better than dry minerals preferably in ambient and humid conditions. Microstructural investigation on the self-healing materials confirms the superficial crack sealing compounds are mainly calcium carbonate based crystals, although different minerals influenced formation of different types of self-healing materials in the inner cross-section of the crack surface.
CEMT 010 100 Encapsulated mineral precursors for self-healing cement based composites  
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Common structural materials undergo a wide variety of defects, due to mechanical or environmental actions. These defects induce damage in the form of cracks which might subsequently collate and propagate leading to strength or durability related issues that will consequently decrease their service life dramatically. This translates to ~£40 billion/year in the UK alone on repair and maintenance of existing, mainly concrete, structures. Existing research on this field suggests, mostly, the use of one or two parts encapsulated resins and adhesives as healing materials. However, in a bulk and widely used material as concrete the use of adhesives and resins raises the issues of cost and health and safety. Our research proposes the use of mineral precursors as healing compounds, which upon release in a discreet crack will react with the surrounding matrix to produce hydration-like products that will heal the crack. The mineral precursors are encapsulated in thin walled soda-lime glass macro-capsules, which in turn are embedded in the cement-based matrix. For this purpose two different types of precursors are being investigated (liquid and powder). The liquid mineral precursor investigated is sodium silicate solution, 40% Na2O(SiO2) in water, and the powder mineral precursor is reactive magnesium oxide. Sodium silicate was marked with fluorescent dye in order to trace its flow and spread within the crack. The specimens were cracked after seven days of curing and left to heal for further 28 days. The efficiency of the precursors was measured in terms of mechanical and durability properties regain as well as in terms of crack area closure. Moreover, healing materials extracted from the crack planes are evaluated through SEM, XRD and FTIR. Results show a good load regain percentage but more importantly the durability indicators show remarkable recovery for the healed specimens compared to uncracked sections.

CEMT 011 164 Can Repeatable Self-Healing Be Achieved in Cementitious Materials?  
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The development of self-healing cementitious materials can open a new world of opportunities for resilient concrete infrastructure under service loading conditions. While self-healing phenomenon has been observed in cementitious materials, questions arise as to whether repeatable self-healing can reliably occur to allow self-repair after multiple damage events. If the self-healing product is dominated by low-strength calcium carbonate it is unlikely to realize repeatable recovery of mechanical properties through this healing mechanism. Even for the recovery of transport properties (aka “sealing”), the localized cracking at the healed region during re-loading will soon deplete the healing agents, ending the healing process. The fundamental hypothesis is that repeatable self-healing in cementitious materials can be possible if a combination of conditions are met: (1) the material exhibits a self-controlled, distributed damage process; (2) a multitude of healing compounds are present that can be randomly triggered by each damage event; and (3) the healing process and reaction kinetics can lead to the formation of high strength and high toughness healing products with sufficiently large volume. In this paper we focus on testing the hypothesis through formulating a new cementitious material system with designed physical and chemical variables. The results can shed light on whether repeatable self-healing can be achieved in cementitious materials.

CEMT 012 253 Capsules changing in brittleness due to leaching of plasticizing agents  
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Although more and more researchers start to investigate the possibility to obtain autonomous repair of concrete cracks by the internal release of encapsulated healing agents, this technique will only become practically applicable if suitable encapsulation materials are developed. To serve this purpose, encapsulation materials need to be first at all to survive the concrete mixing process, while after concrete hardening, they need to become brittle so they easily break and release their content upon crack appearance. In the current study, polymeric capsules made from ethyl cellulose were modified by four different plasticizing agents (triacetine (TAC), triethylene glycol diacrylate (TEGDMA), dibutyl sebacate (DBS) and polyethylene oxide (PEO)) to make them become more flexible. Addition of these modified capsules during the concrete mixing process proved that for increasing percentages of the plasticizing agent, the capsules became less fragile and could more easily survive the mixing process. Evaluation of the capsules after exposure to an alkaline solution, demonstrated that the capsules become more brittle after some time due to diffusion and hydrolysis of the plasticizing agent. However, the bond strength between these capsules and the cementitious matrix seemed not high enough to cause capsules breakage instead of pull-out of the capsules. In addition, leaching of some of the plasticizers led to the formation of acids, which reacted with the surrounding cementitious matrix, causing degradation, while other plasticizers under investigation seemed to react with the healing agent inside the capsule. Moreover, the capsule wall did not seem to be tight enough in order to prevent premature hardening of the encapsulated healing agent. Therefore, the proposed combination of ethyl cellulose with TAC, TEGDMA or PEO seemed not to be appropriate for use in self-healing concrete. In the future different polymeric materials and plasticizing agents will be combined and if necessary multi-layered capsules will be considered in order to combine good bond properties and tightness with flexibility of the capsules.

CEMT 013 190 Materials for Life (M4L): Combining multi-scale healing techniques in cementitious materials  
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Trupti Sharma, University of Bath, UK  
Antonio Kanellopoulos, University of Cambridge, UK  

The Materials for Life (M4L) project team are developing a multi-scale system using a range of interdisciplinary technologies to promote and enable self-healing in cementitious materials. The three-year UK Research Council funded project, which began in July 2013, is collaboration between Cardiff University, University of Cambridge and University of Bath. The project has now reached the point where the integration of the individual techniques, developed at each University, is being investigated. The individual healing techniques that are being considered are intended to address damage at various length and time scales and are encapsulated healing agents, bacterial healing, crack closure using shape memory polymer (SMP) tendons and vascular networks with the ability to supply healing agents on a repeated basis. The challenges encountered in amalgamating the techniques to form a multi-scale healing system are presented. The different combinations considered are encapsulated bacteria, an encapsulated mineral precursor used with SMP, bacteria delivered using flow networks and flow networks supplying healing agents in combination with the SMP. The results provide a first indication of the overall performance of the combined systems and the interaction between the various healing processes. It is proposed that a combination of these systems, applied in different scenarios, can give a whole-material response to damage at a range of spatial and temporal scales and has the potential to improve the efficiency of the individual techniques. To be a truly self-healing material, the integrated components will need to act synergistically in order to reduce or remove the requirement for inspection, maintenance, repair and replacement of construction materials over the life of a structure, creating a genuine material for life.
Natural fibres are a waste product of food and agriculture industry to which a great potential of use as dispersed reinforcement in cementitious composites has been recognized, making them a valuable source of income for developing communities and countries, where they are abundant and can be harvested with minor investments. A further value to the use of natural fibres in cementitious composite is promoters and facilitators of self-healing phenomena has been recently hypothesized and confirmed by preliminary investigations. As a matter of fact, thanks to their porous microstructure, natural fibres are able to create a porous network through which the moisture, as absorbed by the same fibres, can be distributed throughout the cementitious matrix and activate the delayed hydration reactions which, together with carbonation ones, can be responsible of the autogenous healing of cracks and damages. In the past years prominent Brazilian and Italian research groups from leading universities have undertaken a comprehensive experimental programme to investigate the efficacy of different types of natural fibres, when used in combination and/or as a partial replacement of industrial fibres (steel), to promote and enhance the self-healing reactions in high performance fibre reinforced cementitious composites. In this paper a thorough microscopical and chemical (by means of TGA) characterization of the cracked/healed surface as well as of the fibre matrix interface has been performed in order to contribute to a deeper understanding of the mechanisms governing the phenomenon. It has been confirmed that the healing reactions are a combination, also as a function of the exposure conditions and age of precracking, of delayed hydration and carbonation: these reactions can occur once the bulk material inside the specimen, which remains unreacted mostly because of the low water/binder ratio characterizing the mix compositions, is exposed, upon cracking, to the atmosphere. The role of natural fibres as vehicles of the environmental moisture inside the bulk material has also been confirmed. Additional healing reaction products forming at the fibre matrix interface, in the case of natural fibres, have been clearly identified, further contributing to the enhancement of the healing capacity of cementitious composites and improved recovery of pristine levels of mechanical performance.

**CEMT 014 281** Microscopic characterization of self healing mechanisms in high performance cementitious composites reinforced with steel
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Paulo Rocha Ferreira, Universidade Federal do Rio de Janeiro, BR

Self-healing technologies are still under development and therefore careful understanding of the mechanisms involved is critical to developing efficient self-healing/self-sealing materials. Water permeation induced self-healing mechanisms in cementitious materials have the potential for sustainable concrete infrastructure. However, recent direct observation of water flow in the narrow gaps showed growth of air bubbles. This research thus examines the water flow mechanisms that lead to air bubble generation in narrow gaps. By using a transparent glass plane bound to a study surface, water flow in the narrow cracks was imitated. Gap sizes of 0.1 and 0.2mm were studied for specimen dimensions of 10 × 17 cm, with a constant water head of 8.5cm in continuous water permeation condition. Video observations, photography and use of coloured water, plus tracer powder revealed water flow profiles before and after air bubble formation and growth. Air bubble growth was observed right from the immediately observable sub-micro size to the large sub-centimetre sizes; and also how this growth shapes water flow profiles within the narrow gaps of two points. At a relatively longer time scale (5 hours), the effect of air bubble creation in terms of gap constriction was observed to cause water flow reduction. Direct observations also revealed that air bubbles could be formed at pore points (surface imperfections of study surface) and are anchored to these points or may be released into the crack where they may remain stable and continue to grow up several millimetres. Observations also reveal the relative stability of these bubbles especially as they grow in size.

**CEMT 015 74** Detailed Observation of Air Bubble Generation by Water Flow Hydrodynamics in Narrow Gaps such as Concrete Cracks
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The United States is facing an unprecedented, and rapidly escalating, infrastructure maintenance crisis. The more than $100 billion spent annually is not enough to keep infrastructure in a state of good repair. More funding, however is only a temporary solution- it is widely acknowledged that new materials, with better durability, are the key to addressing this significant challenge. The electrochemical corrosion of rebar in steel-reinforced concrete is a major contributor to this maintenance crisis. One of the most popular methods of delaying the onset of corrosion is to use epoxy-coated rebar (ECR). Chips or cracks in the epoxy coating, which can be easily introduced during handling or at the work site, significantly reduce the effectiveness of this technique. This research focuses on the development of self-healing coatings for rebar. Specifically, self-healing coatings containing encapsulated tung oil have been investigated for structural rebar. The healing ability has been characterized by accelerated corrosion testing. The impact of self-healing coatings on steel-reinforced concrete mechanical properties has also been evaluated. Additionally, microscopy was used to characterize the self-healing coatings as well as the interfacial transition zone between the coatings and cement. The corrosion tests have been run on large-scale specimens that can easily be scaled up further.

**CEMT 016 218** Investigation of self-healing rebar coatings for reinforced concrete
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The durability of concrete can be affected by the ingress of chlorides, carbon dioxide and other harmful agents. Cracking of concrete formed by early-age shrinkage, environmental conditions or mechanical loading forms paths for these agents. Closure of early-age cracks and restriction of future crack growth would improve the durability of concrete structures. Feasibility studies have been carried out previously for a shape-memory polymer (SMP) system to close cracks in small mortar beams, with resulting improvements in autogenous healing of the mortar compared to control samples. This paper presents experiments undertaken to upscale this work using SMP strips in larger concrete beams to produce a delayed prestress, considering the effect of this prestress on the autogenous healing of the specimens after varying durations of post-damage curing. The proposed system uses heat-activated SMP strips embedded into prismatic beams made from a structural concrete mix. Experimental results and qualitative evidence of crack closure performance and autogenous healing are presented. Self-healing is quantified by repeated flexural loading of the samples after submerged curing. Details of planned work to further upscale the system in preparation for site-based trials of the system are presented.

**CEMT 017 63** Shape Memory Polymer (SMP) Prestressing System to Enhance the Autogenous Healing of Structural Concrete
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The durability of concrete can be affected by the ingress of chlorides, carbon dioxide and other harmful agents. Cracking of concrete formed by early-age shrinkage, environmental conditions or mechanical loading forms paths for these agents. Closure of early-age cracks and restriction of future crack growth would improve the durability of concrete structures. Feasibility studies have been carried out previously for a shape-memory polymer (SMP) system to close cracks in small mortar beams, with resulting improvements in autogenous healing of the mortar compared to control samples. This paper presents experiments undertaken to upscale this work using SMP strips in larger concrete beams to produce a delayed prestress, considering the effect of this prestress on the autogenous healing of the specimens after varying durations of post-damage curing. The proposed system uses heat-activated SMP strips embedded into prismatic beams made from a structural concrete mix. Experimental results and qualitative evidence of crack closure performance and autogenous healing are presented. Self-healing is quantified by repeated flexural loading of the samples after submerged curing. Details of planned work to further upscale the system in preparation for site-based trials of the system are presented.
Concrete is an important building material, due to its ease of use and relatively low cost. However, the presence of cracks endangers the durability of concrete and can result in reinforcement corrosion, since a pathway for harmful particles dissolved in fluids and gases is generated. Manual repair costs can go up to half of the annual construction budget. Instead, introducing a superabsorbent polymer (SAP) during concrete mixing can create a self-sealing and -healing material. Some SAPs undergo major characteristic changes by small environmental variations. These so-called 'smart' polymers have the ability to sense environmental stimuli. The use of pH-responsive SAPs can be extremely useful for the envisaged application (i.e. self-sealing and self-healing of cracks). When cracks in concrete are subjected to external wetting, ingress of moisture will cause the SAP to swell. When the external fluid possesses a low ionic strength, the SAP will swell to such an extent that it completely fills the crack and slow down or even prevent the further infiltration of water. In addition, these polymers may promote autogenous healing. The proposed paper discusses the effects of a plethora of pH-responsive SAPs. First, the SAPs have been characterized by means of attenuated total reflectance-infrared (ATR-IR) spectroscopy and high resolution magic-angle spinning (HR-MAS) 1H-NMR spectroscopy. In addition, the sorption and desorption of moisture at different relative humidity have been measured through dynamic vapour sorption (DVS) experiments. Furthermore, their swelling capacity at varying pH-values in aqueous solutions and (acidified) cement filtrate has been compared. In a second part, the mechanical properties of mortar mixtures with(out) SAPs have been assessed by performing flexural and compressive strength tests. The sealing efficiency has been measured through a water permeability set-up. The results indicate that these newly developed polymers are promising for their crack-sealing and -healing potential in concrete.

Evaluation of the self-sealing effect of mortar containing polymeric healing agents

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In many studies on autonomous healing, evaluation of the self-healing efficiency focuses on the regain in mechanical properties. However, for a lot of structures like tunnels, liquid containing structures, etc., regain in liquid-tightness is the most important evaluation criterion. Within the HEALCON project, two different tests were developed by TU Delft and U Gent and are recommended in order to quantitatively evaluate the sealing efficiency on lab scale. These tests evaluate whether the passage of water through the crack is blocked by the healing agent. (1) sealing assessment via water flow: The test is performed on cracked and water-saturated mortar prisms, containing a hole in the middle crossing the crack. Water under pressure is provided to the hole and the leakage from the (healed) crack is monitored in function of time. Comparison between the results of cracked-unhealed and cracked-healed specimens allows one to quantitatively evaluate the sealing efficiency. (2) Sealing assessment via capillary water absorption: Cracked mortar prisms which are partly waterproofed (leaving the area surrounding the crack exposed) are put in a 5 mm deep water bath and the mass of absorbed water is monitored in function of time. Based on the sorption coefficients obtained for uncracked, cracked-unhealed and cracked-healed specimens, the sealing efficiency is evaluated. The test methods described above were applied to three different self-healing mechanisms studied in HEALCON and the techniques were found suitable. In the extended paper, the results obtained with the polymeric healing agents (superabsorbent polymers and elastic polymeric healing agents) will be discussed in detail. The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n°309451 (HEALCON).

Autogenous healing of cementitious materials promoted by superabsorbent polymers studied by means of X-ray microtomography

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Autogenous healing of cracks may offer a solution for brittle cementitious materials. Further cement hydration and calcium carbonate crystallization will hereby heal the cracks if sufficient building blocks and water are present. The building blocks are available through the well-designed mixture with a low water-to-binder ratio and water is available through the inclusion of superabsorbent polymers. These polymers are able to extract moisture and fluids from the environment and to provide it to the cementitious matrix for autogenous healing. This healing will lead to the regain in mechanical properties, as already found in previous research. As the crack seems to be completely visually closed at the surface, one may ask whether this healing also is present in the interior of the crack. X-ray computed microtomography was therefore used to study the extent of autogenous healing in cracked cylindrical specimens after autogenous healing. It was found that the autogenous healing in a cementitious material is dependent on the crack depth. Only the first part of the crack is closed by crystal formation in case of wet/dry cycles. In combination with superabsorbent polymers, the extent of healing was more substantial, even in the interior of the crack. There was even partial healing in the interior of the crack when stored at a relative humidity of 60% or more than 90%, but only in mixtures containing superabsorbent polymers. The smart cementitious material with superabsorbent polymers thus is an excellent material to use in future building applications as the healing extent is improved.
Self-healing of concrete cracks is a potential way to increase durability of structures. Even if the natural or autonomic healing capacity of concrete is rather well understood, both from a mechanical and a permeability point of view, non-destructive techniques are required to supplement destructive tests assessing and monitoring the healing efficiency. A technique that can precisely quantify the healing state of small cracks is needed as an alternative to microscopic observation. In this study, a novel non-destructive technique, based on the analysis of the late part of ultrasonic signals (Coda), is developed. The method, relying on nonlinear acoustic mixing of coda waves with lower-frequency swept pump waves, can provide an efficient global detection of small cracks in cementitious materials. By simultaneously comparing, for both uncracked and cracked mortars, the ultrasonic velocity variations and decorrelation coefficients between the unperturbed and perturbed signals with pump amplitude, it is possible to accurately detect cracks with widths as small as 20 µm, associated with velocity variations of approximately 0.01%. Moreover, velocity variation and decorrelation coefficients are proportional to the crack width. Healing quantification is then possible by monitoring the evolution of the non-destructive parameters along time. After immersion of the specimens to heal with uncracked reference specimens, the comparison between microscopic and non-destructive measurements shows that the non-destructive technique proposed is sensible to healing. The influence of the pump excitation on the velocity variation and the decorrelation coefficient is drastically decreased after healing, revealing the filling of the crack by a solid material. Although further research is needed to implement this technique on larger structures with multiple cracking patterns, the global information it provides can be considered as a good durability indicator.

**CEMT 022 81** Proof of efficiency: Examination of concrete beams with self-healing properties by non-destructive testing methods

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The research and design activity of self-healing mechanism in terms of concrete is constantly increasing. Apart from the basic principle of self-healing concrete to show waterproof-concepts to avoid reinforcement corrosion, thus to prolong the lifetime, a consideration and characterization of the proposed healing method is necessary for each relevant practical case study. In a large research project founded by the European Commission different healing agent concepts like bacteria, hydrogels and (bio-) polymers for varying application fields are in development. To commercialize and achieve market acceptance a proof of efficiency of the healing process is required. To monitor and verify the healing effect of construction elements (e.g. large beams, retaining walls, basement) in-situ non-destructive testing methods have obvious advantages in opposition to destructive methods. Since the start of the project in 2013 first successful results of non-destructive testing methods have been obtained in a laboratory scale. The interaction between crack formation and capsule breakage is one essential factor for the efficiency of crack repair. Therefore crack-controlled three-point bending experiments, monitored by acoustic emission technique, have been conducted. Applied ultrasonic measurements for monitoring the curing process provided the evidence of crack sealing. Furthermore, these insights can be used for modeling (delivery of material data like elastic moduli, etc.) and, on the other for characterization of material properties of the healing agents (stability, hardening, etc.). The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 309451 (HEALCON).

**CEMT 023 252** Experimental study on self-healing effect against freeze/thaw cycles of FRCC with PVA fibers and additives

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According to previous researches by the authors, it was confirmed that fiber reinforced cementitious composites (FRCC) using synthetic fibers (e.g. poly vinyl alcohol; PVA) has a great capability of self-healing of cracks. In this study, extra dosage of PVA as an additive was tested. Experimental studies were carried out to evaluate the self-healing capability against freeze/thaw cycles according to RILEM CDF/CIF method. The damaged FRCC specimens were immersed in water bath for self-healing curing. In order to evaluate their self-healing capability, dynamic Young-modulus measurement, water permeability test and microscopic observation were then carried out. As a result, it is confirmed that the chemical precipitation on the crack surface of the damaged FRCC specimens, the admixture of PVA might be expected to enhance the self-healing capability of cracks.

**CEMT 024 231** Analysis of Self-Healing Potential of Advanced Cementitious Composites – Preliminary Compositions and Experimental Results

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The imperative need for environmental sustainability generally leads to energy and resource saving measures, including in the construction branch, where concrete and cement based composites are the most used building material category and, as consequence, they induce significant costs for maintenance and repair works of their inherent, time dependent, degradation. The goal of concrete durability improvement, enhancing the service life of concrete structures, is clearly related to cracks appearance and evolution within the cementitious material and possible methods to ameliorate them, for failure prevention. Along the time, there was noticed a certain ability of cementitious materials to autogenously heal themselves, which implies an economical and minimum invasive environmental approach to limit concrete structures degradation. The improved self-healing potential of Engineered Cementitious Composites (ECC), a special category of High-Performance Fibre-Reinforced Cementitious Composites (HPFRCC), was considered to be the basic, inspiring nuclei for development of similar compositions, using local, Romanian or East-European raw materials (silica sand, powder type wastes and industrial by-products as additions, cement, etc.). The paper presents the initial experimental procedure for evaluation of self-healing potential of the prototype compositions, considering both aspects: crack closing and also physical mechanical properties recovery after exposure to wet and dry conditioning cycles.
Crack is inevitable for concrete infrastructures during their service life. The presence of crack reduces the mechanical properties and bring potential safety hazard to infrastructure. In this study, the influence of self-healing on the ECC’s (Engineered cementitious composite) tensile properties was investigated. ECC is a new kind of HPRRC, featuring high strain capacity of 3-5%, accompanying with sequent multiple micro-cracks development, meanwhile maintains very tiny crack width (about 20 μm in this study). The dog-bone shape specimens used in the tensile test were pre-loaded to the tensile strain level of 1%, 2%, 3%, 4%. After that, to achieve micro-cracks’ self-healing, the pre-loaded cracked specimens were immersed in the water, undergoing wet-dry cycles. And then, the self-healed specimens were reloaded under tension. The results show that ECC can still have high tensile strain capacity of 4% and more than 90% of ultimate tensile strength after healing. The first crack strength recovers to 50% of original cracking strength, and the stiffness recovery ratio of cracked-specimens ranges from 58% to 92%. It seems like self-healing products fill the cracks, forming new composites together with fibers bridging cracks surfaces, thus help the recovery of tensile properties.

With the tensile mechanical properties recovery caused by its self-healing behavior, ECC can be a resilient material in the application of infrastructures.

CERAMICS & METALS

CM+MT 01 155 On the decomposition behaviour of MoSi2 and B-doped MoSi2 sacrificial particles in self healing yttria stabilized zirconia coatings
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Yttria stabilized zirconia coatings are often applied as a thermal barrier in high temperature and harsh environments that is encountered in e.g. gas turbine engines. Combustion chambers, blades and vanes provided with such coatings suffer from delamination crack damage due to stress caused by mismatch in coefficient of thermal expansion and poor damage tolerance of the intrinsically brittle zirconia ceramic. Hence, the lifetime of this ceramic coating is limited. Therefore, a mechanism with crack healing at high temperature is desirable, in order to extend their lifetime and enhance their reliability. A viable option to create a self-healing zirconia coatings is to incorporate Mo-Si based healing particles into the matrix, so that when cracking occurs these sacrificial particles will react at high temperatures with oxygen to form a viscous SiO2, which fills and close the crack. In addition, the healing agent reaction product (i.e. SiO2) itself reacts with zirconia matrix to form well-adhering ZrSiO4 at the original crack-surface interface. The chemical reaction between SiO2 and zirconia is a vital step for the healing process. The final product ZrSiO4 restores the mechanical integrity of zirconia matrix. Hence, the kinetics of ZrSiO4 formation from zirconia and Mo-Si based intermetallic particles is studied. Earlier work has demonstrated that the concept works, but comprehensive information on the kinetics of self-healing mechanism is lacking. Therefore, the self-healing reaction with MoSi2 (without and with Boron) based dispersed sacrificial particles in zirconia matrix was investigated at 1100 and 1200 °C, respectively. The kinetics of ZrSiO4 formation is dominated by the diffusion of the reacting species rather than the chemical reaction. The rate of zircon formation at 1200 °C is about three times higher than that at 1100 °C. At 1100 °C the addition of 2 wt% Boron in the MoSi2 particles effectively promotes the formation of the amorphous SiO2 and thereby accelerating the reaction rate by a factor of two (see Fig.1). Thus, MoSi2 doped Boron is attractive as a healing particles in zirconia ceramics.

CM+MT 02 71 Cyclic Thermogravimetry Analysis of ceramic-intermetallic composites prepared by SPS for a new self-healing TBC
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The SAMBA project deals with the creation of a new design, unique self-healing thermal barrier coating (TBC) for gas turbines and other thermally loaded structures in order to realize a significant extension of the lifetime of critical high-temperature components. The concept is based on novel AI2O3 coated Mo-Si particles embedded in the TBC layer, typically consisting of yttria-stabilized zirconia. MoSi2 particle-yttria stabilized ZrO2 matrix composites with high density (97%) were prepared by using Spark Plasma Sintering (SPS) and their oxidation behavior under thermal cycling was characterized by using Cyclic Thermogravimetry Analysis (CTGA). CTGA is a thermo-mechanical test which was used for the first time on a composite material in this project. Large mass gains were measured as a result of the oxidation of the MoSi2 particles embedded in the YSZ matrix. This was explained by the fact that the reactive surface of the particles is very large when compared to the typical surface of a MoSi2 bulk material. This allowed a precise measurement of the MoSi2 powder oxidation kinetics, once the reactive surface area was determined by image analysis. These oxidation kinetics were then compared with the oxidation kinetics of the bulk MoSi2 material. This allowed to determine how the embedment of the powder and the healing reaction of the formed silica with the surrounding zirconia, modified the oxidation kinetics.

CM+MT 03 145 Selection of Mn+1AXn-phase ceramics for autonomous healing of crack damage
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MAX phase ceramics, atomically layered ternary carbides and nitrides, have a range of advantageous properties that make them attractive candidates for high temperature applications, where the material is exposed to thermal cycles, mechanical loading and oxidation. Additionally, autonomous crack healing has been reported for two of the Mn+1AXn[MAX] phase ceramics, i.e. Ti2AlC and Ti3AlC2. The desirable healing behaviour is due to the formation of a stable, well-adhering oxide with a high relative volume expansion and having mechanical properties close to those of the matrix. The present analysis aims to predict the occurrence of similar autonomous high-temperature crack-healing behaviour in other MAX phase materials on the basis of postulated primary and secondary criteria analysing their reported thermodynamic, thermo-kinetic and mechanical properties: preferential oxidation of the A-element, fast diffusion of A-element, volume expansion upon oxidation and adhesion of the oxidation product to the matrix. The analysis correctly identifies Ti2AlC and Ti3AlC2 as suitable MAX phase variants for autonomous high-temperature crack healing. Also other Al-containing MAX phases seem promising, of which Ti2AlC and V2AlC were identified and of the Si-containing MAX phase compounds Ti3SiC2 met the criteria for autonomous high-temperature crack healing.
The mainstream research on self-healing ceramics for the last decade was new developments of advanced self-healing ceramics. On the other hand, discussions about essential factors in order to put self-healing ceramics into practical use, such as "design stress" or "durability", have been disregarded. In this paper, the discussion on durability was focused and the lifetime of alumina/ SiC composite ceramics, which is the most widely investigated self-healing ceramics, was studied. Crack healing of alumina/ SiC is induced by oxidation of embedded SiC particles called self-healing agent. The expression of self-healing is limited by temperature because the enough formation of SiO2 for filling cracks requires the heat treatment above 1200 °C. However, at such a high-temperature region, internal oxidation layer (SiO2+Al2O3) also will grow due to inward oxygen diffusion, as shown in Fig.1. Since self-healing cannot be expressed at the layer due to absence of self-healing agent, durability of alumina/ SiC can be described as a function of growth of internal oxidation layer. Therefore, the authors defined the lifetime as a minimum time when the internal oxidation layer thickness reaches 20 µm, which corresponds to the allowable crack size of alumina/ SiC. This value is determined on the basis of a nonlinear fracture mechanics. To validate the definition, the constant ~60 µm depth pre-cracks were introduced by Vickers indenter into the pre-heat-treated specimens having 10 to 60 µm internal oxidation layer, and subsequently the specimens were heat treated in ideal crack-healing condition (1300 °C 1h). Then the strength recovery rates were measured by bending test and healed-crack areas were observed by FE-SEM or EPMA. According to the results, indeed the strength recovery rates were reduced as a function of internal oxidized layer thickness. Furthermore, based on the results, we established the methodology for lifetime estimation by evaluating the temperature dependence of internal oxidation layer growth rate.

New healing agents for high temperature alumina ceramics delivering mixed oxides
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In recent years healing of crack damage in structural ceramics for high temperature application has been realized by embedding 15 vol.% SiC sacrificial particles that produce a single oxide upon oxidation as shown in Fig.1 (a). However, the formation of SiO2 to sealing the crack requires relatively high temperatures (above 1200 °C). In order to enable crack healing at lower temperatures, the use of Ti containing sacrificial particles is explored, e.g. TiS2 and TiSiC2. In these composites the resulting crack filling substance is a mixture of two oxides, viz.: TiO2 and SiO2 as shown in Fig.1 (b). In this case the crack filling and strength recovery not only depends on temperature and time but also on the concentration of Ti and Si in sacrificial particles. To study the effect of TiO2 in the healing agent, the self-healing behavior of composites containing mixed-oxide forming particles, i.e. TiS2 and TiSiC2, was compared with the self-healing behavior of composites containing particles forming a single oxide, i.e. TiC and SiC. The relative volume expansion upon oxidation of the healing particle and the work of adhesion of self-healing agent with the matrix were calculated. Next, the oxidation kinetics of the sacrificial particles, which is determining the crack gap filling kinetics, was investigated with thermogravimetry analysis (TG-DTA). Further, the strength recovery of pre-cracked self-healing composites was investigated using bending tests. Finally, the healed-crack areas were investigated by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). The composites with Ti containing sacrificial particles can be healed already at 600 °C and higher.

Self-healing of creep damage in Fe-Au and Fe-Au-B-N alloys
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When exposed to moderate stress levels at elevated temperatures for long times steel components can exhibit premature and low-ductility creep fracture, which arises from the formation, growth and coalescence of (initially) nanoscale pores at the grain boundaries. Self-healing is a promising new approach to enhance the component lifetime. We demonstrate that self-healing is achieved by precipitation of substitutionally dissolved Au atoms in the iron lattice on the creep cavity surface, slowing down or even stopping further growth. In our initial studies on thermal aging of pre deformed Fe-Au and Fe Au B-N alloys a clear defect-induced Au precipitation was observed. Soluble Au is found to exclusively precipitate on deformation-induced defects. In the present study, creep behaviour and microstructure evolution is studied for different applied stress levels at 550 °C. The creep lifetime of the solutionized Fe-Au alloy is compared to the solutionized and solution depleted Fe-Cu alloys in order to clarify the healing efficiency of solute Au atoms in the Fe matrix. The mechanism for the improved creep lifetime is clarified by microstructure studies of the Fe-Au and Fe Au B N alloys after creep. Combined Electron Microscopy (SEM & TEM), Electron Backscatter Diffraction (EBSD), Electron Probe Micro Analysis (EPMA) and Atom Probe Tomography (APT) were used to characterize the site-selective segregation process of Au at creep cavities and cracks. For lower stress levels, pore filling fractions of up to 80% have been observe.

Self-healing of Multifunctionality in Metal/Oxide Hybrid Materials
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Al2O3-based hybrid materials dispersed with nano-Ni particles, Ni/Al2O3, are promising structural materials with high mechanical strength and improved fracture toughness. Ni/Al2O3 hybrid materials have self-healing function for surface cracks via high-temperature oxidation process. Mechanical strength of Ni/Al2O3 hybrid materials can be recovered via high-temperature oxidation even if the surface is cracked. As well gas-tightness of Ni/Al2O3 hybrid materials can be also healed via high-temperature oxidation. In the present report, self-healing of multifunctionality in Ni/Al2O3 hybrid materials is discussed. Other materials systems are also discussed on their self-healing of multifunctionality.
Steel used in turbines and steam pipes suffers from creep damage when subjected to constant loading conditions at high temperatures. Creep cavities grow and eventually coalesce, which eventually leads to failure. The relatively slow creep deformation and the exposure to high temperatures make it possible to design precipitation reactions that can act as a self-healing mechanism. Self-healing of creep damage has recently been demonstrated for Fe-Cu and Fe-Au alloys at a temperature of 550 °C. The alloying atoms in supersaturated solid solution, can form precipitates at the sites where the creep cavities form. This significantly slows down the damage formation and increases the time to ultimate failure.

In this study a wide range precipitation reactions for this type of self-healing behaviour is reviewed in order to design an optimally self-healing iron-based alloy. This is done by applying modelling techniques both on a micro- and atomic scale. Diffusivities of a wide range of impurity elements in ferritic iron are computed through Density Functional Theory (DFT) techniques. A finite-element model was used to evaluate the filling of creep cavities by precipitation for different solute elements. Apart from the diffusivity of the element in the bulk and along grain boundaries, the solubility was shown to play a significant role as well. The self-healing potential of ferritic iron-based alloys systems under different temperature and loading conditions was evaluated using diffusivities of potential solute elements in combination with their segregation energies and solubilities.

Self-healing ceramics can attain complete strength recovery due to oxidation induced self-healing. The super healing effect gives self-healing ceramics ultimate high strength integrity. As well-known, ceramic components cause large strength degradation with cracking due to low fracture toughness. The feature makes lifetime of ceramic component be determined by the probability of occurrence of overload events, such as crush and thermal shock. In contrast self-healing ceramics can be used until self-healing ability is degraded by oxidation diffusion. The time dependent lifetime expand the application of self-healing ceramics. Recently the present authors succeeded to develop fiber-reinforced self-healing ceramics (shFRC) to apply the turbine blade in jet engine. Moreover, new types of shFRCs have been developed for engine components of automobile. In the present paper, the application road map summarizing these applications of self-healing ceramics will be shown.

Massive material loss of jet engine turbine components as a result of volcanic ashes or sand erosion will reduce the efficiency of the engine and impair the flight safety potentially leading to machine failure. Healing of the surface cracks, which precede the actual erosion process, as a result of a crack filling oxidative high temperature reaction may reduce the erosion rate and prolong the lifetime of turbine engine blades and vanes. Cr2AIc MAX phase is a promising material for application in an aero-engine. This material can withstand the harsh environment due to its resistance to high temperature oxidation and thermal shock. Recently, self-healing of relatively large cracks of 2.5 mm length and 2 μm width in this material by high temperature oxidation has been demonstrated. Yet, healing of emerging erosion damage in Cr2AIc ceramic is to be demonstrated. Bulk Cr2AIc ceramic plates were subjected to room temperature erosion for 10 minutes using glass microbeads accelerated to 110 m/s and impinging perpendicular to the sample surface. After the usual incubation time, the erosion rate reaches a constant rate, which is associated with the formation of network of small cracks underneath the surface. Next, the material was annealed at 1200 °C for 10 min in air resulting in the closing up of the network of small cracks due to the formation of well-adhering Al2O3. The subsequent erosion rate of the healed Cr2AIc ceramic at room temperature is drastically reduced. Experiments on samples containing various porosity leaves shows that the improvement in erosion resistance is due to the healing of the surface crack network as well as the filling of the pores. As shown in Figure 1, both factors leading to a substantial increase in the erosion resistance.

**COATINGS & PAINTS**

**COAT 04 42 Interfacial healing of hybrid sol-gel based polymers containing thermo-reversible tetra-sulphide groups**

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Various intrinsically self-healing (SH) polymers relying on triggered/spontaneous reformation of chemical/physical bonds have been presented in literature. Recently the authors have presented a healable hybrid sol-gel based polymer. The developed system consisting of epoxy-alloysilanes containing thermo-reversible tetra-sulphide groups shows remarkable macroscale damage closure capabilities upon mild thermo-mechanical stimulus with an optimal healing kinetics at 70 °C.

In this work, the properties of the developed SH polymer were mechanically and spectroscopically evaluated. The bulk viscoelastic and mechanical properties of the SH sol-gel based polymer were measured by dynamic mechanical-thermal analysis (DMTA) and static tensile tests. In addition to the standard tensile experiments, fracture tests were performed using single edge notched tensile (SENT) geometry to evaluate the interfacial healing efficiency. The effect of the healing temperature and time on the healing performance was also investigated. Additionally, application of the SH sol-gel based polymer as a protective coating for AA2024-T3 is presented. The sealing efficiency of the scratched samples and hence the ability of the coating to recover its barrier functionality was determined by performing electrochemical impedance spectroscopy (EIS) tests on the scratched and healed samples. The tensile and fracture tests demonstrated a recovery of the original mechanical properties up to 65% upon annealing at temperatures below 75 °C. Upon application of moderate temperatures and pressures, the coating system showed enough mobility to close 300 μm wide scratches, while keeping its overall integrity. The fully healed coatings showed impedance modulus as high as intact coatings for long immersion times demonstrating a sustained healing at the damaged site. The current system shows encouraging results and might provide the basis for the first generation of intrinsic healing sol-gel based coatings for corrosion protection.
COAT 02 181 Acrylate-based UV-cured self-replenishing hydrophobic coatings for further industrial applications
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Most of the hydrophobic coatings currently available are vulnerable in maintaining their hydrophobicity upon surface damage or wear, due to the irreversible loss of the low surface energy chemical groups. Therefore, the concept of self-restoring hydrophobic functionalities on polymeric surfaces, by replenishing spontaneously the functional groups on the damaged surfaces, is of high interest for the coatings industry. The proof-of-principle of self-replenishing hydrophobic surfaces was previously reported for a "model" system based on a Poly(urethane)-based cross-linked soft (low-Tg) network with a small amount of fluorinated dangling chains. In these systems the low surface energy dangling chains can re-orient towards the new air/coating interfaces created upon damaged. Further studies on these self-replenishing model systems, using a dual experimental-simulation approach, revealed details of the influence of the network parameters on the surface-segregation and self-recovery mechanism. However, the clear drawbacks identified for this model system will restrict its direct industrial application: 1) the current cross-linking procedure involves high temperature and long curing time, 2) the use of fluorinated materials is expected to be limited or completely banned due to health and environmental concerns and 3) these systems have rather weak mechanical properties, e.g. low hardness (due to low Tg) and low solvent resistance. In this work, we present a new approach for self-replenishing systems which will be more industrially applicable. More cost/energy-effective self-replenishing hydrophobic polymer coatings were prepared by incorporating methacrylate-terminated fluorinated dangling chains into polyethylene glycol diacrylate (PEGDA)-based networks via UV-initiated radical polymerization. The prepared coatings exhibit multiple self-replenishing ability of the surface hydrophobicity after microtoming. We will discuss how the network architecture and the significantly accelerated UV-curing process influence the self-replenishing behavior.

Acknowledgement: This research forms part of the research programme of the Dutch Polymer Institute (DPI), project #758 (SER-LED).

COAT 03 91 USE OF CONFOCAL RAMAN AND LOCALIZED ELECTROCHEMICAL METHODS TO STUDY MULTIPLE SELF HEALING ACTIONS IN CORROSION PROTECTION COATING
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Corrosion of metals can best be avoided using a barrier coating preventing aggressive species from reaching the metallic substrate. However, if the barrier is broken, corrosion inhibitors need to foresee the protection of the metal. Therefore, corrosion inhibitors are often incorporated in the coating matrix. But even "smart" containers, which leach corrosion inhibitors only when a corrosive attack takes place, do not offer the same year-long protection of a barrier coating. In the last decade, self-healing or self-repairing coatings have been developed, which re-establish the coating barrier – either autonomously or based on for example a thermal trigger. However, for the time until the coating is repaired or when the repair is insufficient, a corrosion inhibition is desirable. Within this paper the authors focus on the use of Raman analysis and several (local) electrochemical methods (EIS, SVET-SIET, SEC) for analysing self-healing coatings, corrosion inhibitor screening methods and possibilities of combining inhibitors with self-healing polymer coatings to achieve a multi-action self-healing coating system. Several polymer and inhibitor systems will be addressed.

Acknowledgement: SURF-VUB is involved in several self-healing projects: SIM-Naprom, SIM-Hints, SHREC and Innoversis- SHARC.

COAT 04 104 Effect of the stoichiometry on the healing capability of an aromatic-aliphatic polyetherimide.
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Various polymers presenting room temperature healing have been reported in literature, mainly using hydrogen bonds and disulphide linkages as the bonds responsible for the healing behaviour. So far the different reported approaches dealt with elastomeric polymers with relatively low mechanical properties. In this work we present a new intrinsic room temperature self-healing polymer with improved mechanical properties for coating applications. The new polymer is based on polyimide chemistry. Traditional polyetherimides (PEIs) are synthesized from an aromatic diamine and an aromatic dianhydride (e.g. 3,3'-oxydianiline and 4,4'-oxydiphtalic anhydride in case of a commercial LaRC-IA) leading to the imide linkage and the outstanding chemical, thermal and mechanical properties of the polyimide family. In this work we have replaced the traditional aromatic diamine by a branched linear diamine made from renewable resources. The resulting polymer polyetherimide (SH-PEI) shows lower mechanical properties (1.20 MPa < σf < 8.80 MPa and 240% < εf < 590%, dependent on the formulation) but was found to have the capability of restoring crack planes at room temperature. The self-healing and general properties of the developed SH-PEI were evaluated as bulk polymers as well as thin coatings on steel plates. The results indicate that the bulk healing efficiencies measured by tensile testing, in terms of ultimate tensile strength after 24 h, are close to 90% at room temperature. These healing efficiencies can be increased when heat is applied. Moreover, the systems show restoration of micron-size scratches leading to the recovery of the barrier properties when applied as coatings. These properties were found to be dependent on the stoichiometry of the two constitutive components.
COAT 05 152 Poly(ethylene glycol)-based hydrophilic networks: model study towards self-replenishing lubricious coatings
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Hydrophilic coatings find many applications in aqueous environments due to the extraordinary properties provided by their high surface energy, e.g., anti-(bio) fouling, anti-fogging, wear comfort, biocompatibility and lubricity. Hydrophilic top coats with lubricious character are particularly important for bio-medical devices which are in contact with the human body and have been widespread applied to increase the patient's comfort and reduce the risk of device-associated infections. The potential reduction of hydrophilic groups at the coating surface, by hydrolysis, wear or temporary exposure to a hydrophobic environments, lowers the lubricating performance. In order to maintain high performance during an increased service lifetime of the coated device, an autonomous replenishing mechanism for restoring the lubricious surface functionality would be desired. Implementing a replenishing mechanism into a hydrophilic lubricious coating requires a profound knowledge of the actual friction behavior of hydrophilic networks. Although hydrophilic network-type coatings have been used since long, the aqueous friction mechanics of hydrophilic networks are very complex and still poorly understood. Therefore a thorough study of the relation between the network parameters, the mechanical properties and resulting friction behavior of well-defined hydrophilic networks is needed, to increase the insights in the structure-property relations of hydrophilic coatings and tune their lubricity properties. In the last decades poly(ethylene glycol) (PEG) has been intensively studied in the bio-medical field for its biocompatibility and anti-protein fouling properties. Moreover, its highly hydrophilic character makes PEG a perfect choice to build-up model network systems for a friction study, consisting of well-defined covalently cross-linked hydrophilic networks. In this work, we report our progress on the study of the influence of the network parameters (e.g., chain length and cross-link density) and processing conditions, on the mechanical properties of well-defined PEG-based hydrophilic networks in relation to their friction behavior. In a following step, this knowledge will allow introducing effectively a self-replenishing mechanism into the hydrophilic network.

COAT 06 246 Design and Characterization of Self-Healing Functionality in Protective Coatings
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The growth of the field of self-healing materials has been accompanied by the development of new chemistries and technologies for coating applications. For aesthetic coating applications, the goal of the self-healing functionality is to help the coating recover its aesthetic properties as fully as possible. The benefit of this capability is obvious for consumer applications where a manufacturer of an electronic device, for example, might differentiate their product from a competitor’s by utilizing a coating with the ability to repair fine scratches that might occur with day-to-day use of the device. Protective coatings present an even more compelling potential for self-healing technologies to the extent that these technologies can contribute to the improvement of the corrosion resistance of these coatings. Since protective coatings are typically designed to exhibit good corrosion resistance, for the incorporation of self-healing functionality into these coatings to be considered beneficial, it must result in a significant increase in the coating’s corrosion performance. In this talk, I will discuss the design of a range of self-healing protective coatings and the use of common standards and test methods to characterize their performance.

COAT 07 112 Stimuli-responsive nanocapsules for self-healing and anticorrosion
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Our group has focused our activities on the synthesis of nanocapsules and nanofibers for self-healing and anticorrosion. We have tailored the chemistry of nanocapsules so that they release specifically one or several corrosion inhibitors and or self-healing agents upon onset of corrosion. Herein, several approaches are introduced, compared, and discussed - including the choice of the stimulus for releasing the active payloads, the complexity of the characterization of the self-healing behavior, and the efficiency of the self-healing.

COAT 08 283 Controlled release of green- inhibitors entrapped in Micro-Spheres (Inhibisphere™TM) for Corrosion Protection in Aerospace
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For more than 20 years, the Aerospace Industry has invested a significant effort into finding a replacement for hexavalent Chromium in anti-corrosion surface treatments. This is especially important in the current regulatory context, where European and national environment policies are becoming increasingly stringent for the chemical industry. The challenge to be overcome by novel protective systems, specifically when applied to large structural parts, is to match the environmental regulation, by avoiding the use of toxic components in formulations, while preserving the required characteristics and performances for the protective coatings in the long term (~ 30 years). Airbus Group Innovations has been actively engaged for the past 15 years in the assessment of new Cr-free healing materials for the corrosion protection of metallic structures. In this project, carried out in the frame of the PESIC collaborative project, partially supported by the French DoD (DGA), we studied the performances of smart containers, called Inhibisphere™, as additives to environmentally friendly paint primers, developed by the French SME MAPAERO (http://mapaero.com/). These containers, developed in partnership between Airbus Group Innovations and the Australian SME Ceramisphere Pty Ltd (http://www.ceramisphere.com/), are submicron ceramic spheres, containing encapsulated green corrosion inhibitors. Ceramisphere’s technology (Inhibisphere™) enables the control of both the size of the particles and their release rate. The Inhibisphere™ have been incorporated by MAPAERO in their paint primers, without any modification to their regular paint production processing. Airbus Group Innovations and the French Laboratory CIRIMAT-ENSIACET were in charge of the assessment of the coatings’ characteristics and performance, on the basis of aeronautical requirements, and of the basic understanding of releasing mechanisms and corrosion behaviour, using electrochemistry. This paper will address the characterization and assessment of the performances of environmentally friendly paint primers, applied by spray on pretreated aluminum surfaces, including different kinds of Inhibisphere™ loaded with green inhibitors. We will compare their characteristics (chemical composition and morphology) and performances, particularly in terms of self-healing behaviour (release efficiency, especially when the coating is damaged) and corrosion behaviour.
Microencapsulation technology has been employed in a wide range of applications such as pharmaceutics, food additives, electronic inks, catalysts, dyes etc. Recently, microcapsules were identified as potential carriers for agents that enable self-healing and enhanced corrosion protection in powder coatings. For this purpose, microcapsules should meet certain requirements such as mechanical stability during application of the coating, free flowing powder form to get a homogenous distribution in the coating, absence of toxic substances etc. The goal of this study is to develop such microcapsules that fulfill the above requirements. For this purpose, so-called drying oils (linseed and tung oil) have been selected as healing agent/core material. These oils are environment friendly and possess the ability to form a film by reacting with the atmospheric oxygen. Microcapsules from melamine formaldehyde were prepared by in situ polymerization, while hydrophilic fumed silica was used to stabilize the emulsion during encapsulation. Current results showed that both linseed and tung oil can be successfully encapsulated by melamine formaldehyde resin. The microcapsules collected were in a free flowing powder form and can be used for liquid and powder coating. The mechanical strength parameters including rupture force and nominal rupture stress were found to vary with their sizes and the amount of shell material. The microcapsules possessed a rough outer morphology and a smooth inner surface. The thermal stability of the microcapsules was assessed by DSC and TGA, and the concentration of silica was found an important factor in getting a stable emulsion and free flowing powder of microcapsules. For the evaluation of self healing efficiency, these microcapsules will be incorporated into the powder coatings, and their self healing efficiency and corrosion protection performance will be monitored by electrochemical impedance spectroscopy, electron microscopy and other techniques.

COAT 010 227 Self-Healing Anticorrosive Coatings via Microcapsules containing UV Curable Epoxy Resin
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Coatings are often used to protect a substrate from corrosion damage. However, the integrity of the coating can be compromised by impact or scratch damage, which exposes the underlying substrate to the corrosive environment. Due to the potential hazards from corrosion damage, self-healing coatings are desirable. A common limitation of previous self-healing approaches is the requirement of human intervention to initiate the healing process. The coatings developed in this work do not require any intervention, making them truly autonomous. In this work, a UV curable self-healing coating to protect steel substrates is demonstrated. A microcapsule based approach is taken, in which capsules containing a UV curable epoxy core are embedded in an epoxy coating. The capsule shell wall material is formulated to protect the core material from UV exposure prior to rupture, so that the healing agent (UV curable monomer) remains active until triggered by mechanical damage. The coating is applied to clean and prepared steel substrates, and ultrasonic analysis is used to measure coating thickness and uniformity. Uniform scratch damage is inflicted on the coating, which ruptures the capsules and allows the UV curable core to fill the damaged region. The damaged region is then exposed to UV light of similar intensity as sunlight, achieving autonomic healing of the damaged coating. Corrosion inhibition efficiencies are evaluated by exposing the healed samples to 5 wt % NaCl solution and using visual inspection and electrochemical linear polarization to quantify corrosion.

FIBER-REINFORCED MATERIALS

FIBR 01 79 Synthesis of Catalysts Immobilized Carbon Nanomaterials for Self-Healing Polymer Composites
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For structural applications, self-healing systems are of great interest because they would allow to overcome not only some difficulties connected to damage diagnosis, but also the appropriate interventions to restore the material functionality. Among the several reported self-healing approaches, the fast and low temperature crosslinking Cu(I)-catalyzed alkyne-azole “click” cycloaddition reaction, and Ru-catalyzed ring-opening metathesis polymerization (ROMP) are valuable. However, catalyst stability and its uniform distribution still remains a challenge. Herein, we have immobilized Cu and Ru catalysts onto the surface of carbon nanomaterials (CNMs) (graphene/CNT) to enhance the stability and dispersion of the catalysts for self-healing processes, including the improvement in mechanical and conducting properties of the resulting composites. CNM supported catalysts represent exceptional characteristic properties, due to their high surface area, thermal stability, and the porous surface, which acts as a scaffold to prevent the agglomeration of the immobilized catalyst particles. The synthesized metal catalysts show high stability at normal reaction conditions (air) including recyclability and reusability, measured via model “click” reactions.

Moreover, the synthesized catalysts show excellent performance for bulk polymerizations as proven via DSC as well as cross-linking processes controlled by melt rheology, designed for self-healing materials. Subsequently, the CNM immobilized catalysts have been evaluated in epoxy based self-healing composites, analyzed by DMA, rheology and DSC.

FIBR 02 225 Manufacturing of Unidirectional Epoxy-Resin/Thermoplastic-Particle Carbon-Fiber Prepreg for Solvent-based Self-Healing
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A unidirectional epoxy-resin/thermoplastic-particle carbon-fiber prepreg is presented for solvent-based self-healing composites. The epoxy resin is a bisphenol-A based epoxy with cyclohexylamine curing agent. Thermoplastic particles [poly (bisphenol A-co-epichorhydrin), PBACE] are incorporated into 3 K carbon-fiber tows. The thermoplastic particles (ca. 1.5 µm) were prepared by the emulsion/solvent evaporation method, and the particles were incorporated into the tow using a fiber sizing process followed by resin impregnation. PBACE particles are distributed uniformly throughout the fiber tows. The amount of thermoplastic phase in the prepreg was controlled by the concentration of thermoplastic particles in the fiber sizing agent. Consolidated composite was then fabricated by hot pressing a prepreg laminate of stacking sequence [0° 90°]S5 at 80 °C for 2 hours followed by 150 °C for 4 hours. The thermoplastic particles were melted and blended into epoxy resin at the processing temperature of 80 °C since the thermoplastic (PBACE) melts at 70 °C, while the epoxy resin remains undercured. The morphology of the thermoplastic phase in the composite is dependent on the cure schedule.
The inclusion of thermoplastic interlayer materials is a well-known strategy to improve the impact resistance and the interlaminar fracture toughness of carbon fibre reinforced polymer composites. However, such interlayers can also suffer unwanted damages such as loss of adhesion leading to a decrease of properties. Self-healing interlayers capable of restoring the loss properties could hence lead to a service life extension. Ionomers are a class of thermoplastic materials that possess the capability of self-healing upon thermal activation as shown for scratches and ballistic impact damage. Moreover, ionomers are also employed as interlayer material in conventional carbon fibre/epoxy composites due to their good adhesive properties. These two characteristics make ionomers interesting materials to be used as interlaminar self-healing systems. The current work describes the development of ionomer interlayers that show healing behaviour by localized heating upon magnetic induction. Localized healing is realized by dispersing ferromagnetic particles into ionomer blends, which are then processed into thin films and applied in composite systems. The dispersed particles locally heat the ionomer film to a temperature that breaks the electrostatic interactions leading to sufficient flow to allow the healing of the material. The approach is demonstrated using the concept of early stage matrix healing where healing is induced during the crack initiation phase instead of when the crack has fully propagated. It is shown that this healing strategy significantly increases the fatigue life of these polymers, which is quantified by traditional mechanical testing procedures (i.e. tensile testing and fatigue testing) before and after induction treatments. Moreover the approach was also employed to restore microscale debonding between the ionomer interlayer and the carbon fibre-reinforced polymer phase. The healing behaviour of the systems was quantified by mechanical testing as well as non-destructive testing (NDT) techniques, such as Nonlinear Reverberation Spectroscopy and the Pulsed Ultrasound Polar Scanning technique.

**FIBR 04 168 Evaluation method of fracture properties of fiber-reinforced self-healing ceramics**

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Fiber-reinforced self-healing ceramics (shFRC) are considered to be most attractive candidate of next generation structural materials using at high temperature, e.g., turbine blade, exhaust component of car engine etc. The shFRC consist of three components, which are oxide fiber bundle, oxide matrix and self-healing agent interlayer. As the self-healing is generated at only the interlayer, it is necessary that crack propagation is led into the interlayer. As a result, shFRC exhibit complex fracture behavior. In order to assess the structural integrity of shFRC, the accurate fracture toughness including the complex fracture manner is needed. In the present study, the fracture toughness and fracture manner of shFRC were investigated by using the beam with Chevron notch. Moreover, the self-healing effect on the fracture toughness was discussed.

**FIBR 05 78 Graphene Supported Copper (I) Nanoparticles for self-healing nanocomposites**

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Self-healing materials including polymer-composites, which have the ability to repair themselves after fracture, have shown a significant attention to use in the industry (e.g. aerospace). A variety of approaches are used to achieve self-healing polymers like capsule-based healing, dynamic covalent bonds, or supramolecular polymer interactions. Graphene, an atomically thick and two dimensional sheet with high Young modulus (1T Pa) and thermal conductivity (5000 w/m.h) is a novel material which can strongly increase the physical and mechanical properties of polymer nanocomposites. The Cu (I)-catalyzed “click” chemistry has been used for organic synthesis and self healing applications due to its efficiency at and below room temperature. In the present study, we report a facile approach for the preparation of recyclable and highly dispersible Cu (I) nanoparticles decorated graphene nanosheets (graphene/Cu(I)), useful as catalysts for the copper (I)-catalyzed “click” reaction as well as for enhancing the physico-chemistry.

**FIBR 06 222 Interfacial Remendability of Glass Fiber-Epoxy Composites Evaluated by Combined Single Fiber Fragmentation and Fatigue Testing**

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The adhesion of the reinforcing fibers to the matrix is vital for the load transfer within a composite. Being able to impart remendability to the fiber/epoxy interface could potentially increase material longevity. Positive results have been obtained by employing the Diels-Alder reaction in a composite of furan-functionalized epoxy-amine polymer and maleimide functionalized glass fiber. In a previous investigation microdroplet pullout testing has shown a healing efficiency of 40% after complete interfacial failure for such systems. In this investigation the healing of single fiber composites with partially damaged interfaces was explored using single fiber fragmentation (SFF) testing combined with cyclic fatigue. A protocol was developed both for partially degrading the interface of a glass fiber / epoxy composite, and for analyzing the healing capability of the damaged interface. Good control of the degree of interfacial damage was achieved by regulating the fatigue load and the number of fatigue cycles. Close to 100% of the interfacial shear strength (IFSS) was recovered in samples when little damage was introduced. Up to 60% healing efficiency relative to undamaged IFSS was measured for samples with moderately damaged interfaces, and up to 48% healing efficiency was observed for samples that had lost a majority of their initial interfacial strength.
We investigated the applicability of a solvent containing capsule repair system to fiber reinforced composite materials. The repair system is based on ethyl phenylacetate (EPA), combined with epoxy, which upon capsule fracture is released on the crack faces, and swells the matrix by diffusion. The healing process is attributed to the reaction of the epoxy functionalities with the unreacted hardener functionalities. Compared to the pioneer DCPD/Grubbs’ catalyst system, this alternative approach is less expensive (absence of catalyst), non-toxic (use of environmentally green organic solvents) and shows full efficiency in pure epoxy samples. Even though this remains a model system, as its stability is not guaranteed at room temperature, this system could be of high interest for composite materials.

We used Vacuum Assisted Resin Infusion Molding (VARI) to produce woven glass fiber-reinforced epoxy resin plates, with a fiber volume fraction of approx. 50 vol% and containing ethyl phenylacetate (EPA)-filled capsules for self-healing purposes, hexyl acetate (HA) capsules as a comparative non-self-healing system, and virgin composite without capsules. The VARI process was successfully adapted as a reproducible and industrially relevant route, leading to realistically high fraction of fiber reinforcement. We investigated the capability of autonomously healing delaminations induced by static loading in Mode I and II. Healing did not take place for any of the composite samples; this was related to the large extent of interfacial delamination and to the reduced EPA diffusion into the matrix in the presence of fibers. Epoxy-rich bonded joints however lead to partial healing. In conclusion, the solvent-based system could be applicable only for healing cracks presenting matrix-rich faces, occurring within resin joints between composites or for matrix microcracks in static or fatigue loading, provided that interfacial failure is not the dominant damage mode.

The authors recently proposed the first autonomous sensing-healing system applicable to large-scale composite structures. This study demonstrates its performance using structural tests. The system combines our fiber-optic-based delamination detection system with a microvascular self-healing material (FIGURE). First, sacrificial fibers (catalyst-impregnated poly(lactic acid) (PLA) fibers [2]) are woven into a dry fabric. After resin infusion and curing, the sacrificial fibers are removed by heating the panel to vaporize the PLA, which yields empty channels in the panel. Cross-sections of these empty channels are then exposed to the panel surface. The panel has a surface sacrificial layer, which does not bear a load, and the channels partially go through the sacrificial layer. By slightly machining the panel surface, one can expose the cross-sections of the necessary channels without damaging the structural layer. Channels are then connected to the main supply tube of a pressurized healing agent through check valves. Meanwhile, shallow holes are created on the other side of the channels, and fiber-optic-based pressure sensors are installed on them. When delamination occurs, the healing agent flows into the channels breached by the delamination and infiltrates the damage for healing. At the same time, the pressure sensors identify the damaged channels by detecting internal pressure changes. This presentation begins by discussing the advantages of the proposed system that arise from its hierarchical nature. The sensing-healing performance is then evaluated using double cantilever beam tests. Finally, the system is applied to stiffened panels to demonstrate its effectiveness under practical conditions.

Delamination damage in fiber-reinforced composites is difficult to detect, challenging to repair, and if unchecked, leads to significant reductions in the structural function of the material. Self-healing polymers and composites offer autonomous methods for repairing damage when and where it occurs through local damage-triggered release of reactive components into the crack plane. However, the self-healing of recurrent damage is difficult because of local depletion of reactive healing agents. To combat this depletion, vascular networks capable of replenishing agents may be incorporated into the material. Here we report self-healing of recurrent delamination damage in a vascular fiber-reinforced composite by incorporating internal vascular networks in the material for repeated delivery of reactive components to a delaminated region. Vascular networks are introduced through vaporization of sacrificial filaments after composite manufacture as described by Esser Kahn et al. Double cantilever beam specimens are utilized to demonstrate complete recovery of fracture toughness over recurring crack opening experiments by pumping healing agents to the crack plane after damage where in-situ mixing of the healing agents occurs and heals the interface. Fluorescent imaging is employed after testing for the visualization of fluorescein-dyed healing agents on the material’s crack plane.

Internal microscopic damage is ubiquitous in fiber-reinforced polymer (FRP) composites that have been subjected to damage, whether this be during the manufacturing process (i.e., via thermal stresses), from machining (i.e., drilling holes for bolted joints), during component assembly or ultimately from in-service loading. Incorporating an in-situ repair solution that can be activated after each of these individual processes could, in the first instance, have a significant impact on reducing composite component scrapage rates, post-manufacture repairs and increase the time period for non-destructive testing (NDT) inspection. Specific industry relevant FRP composite component features have been investigated and re-engineered to incorporate an in-situ repair mechanism. Self-healing agents were embedded into carbon and glass FRP prepreg-based laminates and tested in double cantilever beam (DCB), open-hole tension (OHT) and skin-stiffener debond specimens; to represent specific areas or design features of high stress concentration where damage predominately occurs during manufacture and in-service. The embedded self-healing agents are thermally activated post-damage to repair the internal structure, akin to the healing functionality in animals and plants. A novel Diels-Alder modified cross-linked epoxy polymer component, synthesised from a combination of multifunctional monomers containing epoxy, amine, furfuryl and maleimide functional groups, was developed and implemented into FRP composite laminates, together with microvascular channels to evaluate a combined Diels-Alder/epoxy-liquid resin approach for healing larger damage volumes via a two-stage repair process. As an initial proof of concept study, results have shown that a material recovery value of greater than 50% fracture strength has been achieved in a high performance prepreg-based FRP composite material using conventional composite manufacturing techniques.
FUNCTIONAL APPLICATIONS

FUNC 01 198 Improvement of strain of vulcanized Isobutylene Isoprene Rubber (IIR) using a heat sensitive ionomeric mechanism
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A normal use of Isobutylene Isoprene Rubber (IIR) is focused on producing a mousse used in motorsport competitions due to its properties of elasticity and damping. Because of normal use of material, cracks inside material appear from internal pressures and temperatures around 100 Celsius degrees.

The objective of this research is the production and evaluation of a polymer based on IIR which is capable to recover autonomously its strain using heat as thermal activation. For this purpose, the mechanism of clusters of ionomers is used to prevent and reduce the appearance and propagation of cracks that limit or collapse the original functionality of the material. The temperature of normal use of the material is used in the ionomeric mechanism to lead to an autonomic self-healing triggering a reorientation of the bonds structure closing partially the formed cracks.

In this research, a mixed polymeric system based on a previous defined composition for IIR with different grades of a selected carboxyl functional ionomer (HYPRO) in weight composition of 1 and 2 % were coupled and vulcanized to low pressures and temperatures in order to have a autonomic self-healing system. A razor blade was used for conducting a crack of 3 mm in the material. For simulating temperature conditions, samples were treated at 100°C during 3 hours. Strain was measuring through tensile strength tests. Ionomer samples recovery was compared to the reference sample recovery. After healing treatment with temperature, a recovery of strain was observed for both grades of IIR-ionomer system of 53 and 66 % respect to reference material recovery of IIR.

Other complementary work conditions and materials are being tested for evaluating different self-healing impacts on IIR.

FUNC 02 113 Stimuli-Responsive Nanocarriers for Self-Healing in Corrosion Protection
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A carrier system is efficient if distinct payloads can be selectively released via different stimuli because unwanted and unspecific release can be avoided. For anticorrosion, the wanted carrier system is the one able to release its self-healing agents or corrosion inhibitors upon change of pH- or/redox-potential due to the variation of these two signals at the corroded sites.

Polymer assemblies loaded with hydrophobic payloads are prepared via self-assembly of amphiphilic copolymers in water. The amphiphilic copolymers are designed to bear a corrosion inhibitor as cleavable side group. The release of the hydrophobic payloads is triggered by reductive cleavage of the copolymer, leading hence to the co-release of the corrosion inhibitor. This property makes the present system advantageous to other polymer assemblies in which the cleaved usually exhibits no functionality. As another stimuli-responsive carrier system, polyamine (PANI) capsules loaded with two different corrosion inhibitors are synthesized via one-pot miniemulsion polymerization and then a surface modification. Unlike previous systems where both payloads are released together, the two corrosion inhibitors could be released selectively and independently by activating the capsules with either pH change or chemical reduction.

Based on the fact that the local condition of the corroded sites provides a change in pH or redox potential, the stimuli-selective release of the multi-payloads makes the nanocarriers promising candidate for corrosion protection.

FUNC 03 86 Effect of filler particle parameters on thermal and mechanical healing of thermal interface materials
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Thermal Interface Materials (TIMs) are widely used as gap-filler materials to improve the heat dissipation of electronic devices. Such materials generally consist of a flexible polymeric matrix highly loaded with thermally conductive particles. The aging of TIMs leading to cracks and delamination generally ends up with the loss of heat transfer and premature device failure. The development of TIMs capable of restoring cracks and delamination would ultimately lead to the recovery of the necessary heat dissipation for a proper device function and hence its service life extension.

In our previous work, we introduced the concept of self-healing TIMs showing both autonomous adhesive and cohesive healing even when loaded with thermally conductive particles. However there is no report on how particle constituent parameters influence the healing ability of self-healing TIMs in particular and self-healing particulate composites in general. In this work the effect of particle size, particle distribution (packing), loading, and particle surface treatment has been investigated.

For the study we used a sol-gel based hybrid polymer as the self-healing matrix loaded with particles with controlled dimensions. The presence of the dynamic disulfide bonds in the organic matrix allows for multiple healing events at relatively low temperatures (between 50 and 70°C). Glass beads of different sizes were first employed in order to evaluate the effect of the particle size (6-160 µm), surface treatment, loading and packing on the healing of the mechanical performance as well as thermal conductivity. Different surface treatments based on silane chemistry were used to increase the particle-matrix interfacial strength as well as its healing potential hence gaining a major understanding of the particle-matrix interface in the healing process of particulate composites. The results show a big dependency of the mechanical, thermal and healing properties on the particle size, packing and loading and less influence of the coupling agents used. In this work, the effect of particles on the healing of particular composites is presented for the first time.

FUNC 04 264 Controlling the Healing Ability of Thermally Reversible Polymer Networks with Light
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The reversible thermoresponsive crosslinking of polymers contributes significantly to the field of smart, adaptive, or self-healing materials and coating applications. [1] A prominent motif for this purpose is the reversible Diels-Alder reaction in which the pair of maleimide (dieneophile) and furan (diene) is the most reliable and investigated. [2, 3]

Herein, we apply our concept of achieving photostimulation over a reversible reaction [4] to polymer networks consisting of thermo- and phoeresponsive furyl-substituted diacylthene crosslinkers and maleimide-containing copolymers (Figure 1).

By turning the Diels-Alder crosslinking reaction “ON” or “OFF” with light, we envision a use of these responsive polymer films in coating applications where the healing ability of the films can be controlled by irradiation with light of different wavelengths.
Nanomaterials are now widely investigated for self-healing applications. One of the most important properties of nanocarriers is their release behavior, i.e., their ability to release selectively self-healing agents upon one or several stimuli with a controlled release rate. Herein, we demonstrate that the control over the release rate of corrosion inhibitor and on the selectivity of the release can be achieved by designing nanomaterials with a hierarchical structure. Redox-responsive silica nanocapsules are first synthesized to allow for an accelerated release of the corrosion inhibitor 2-mercaptopbenzothiazole as payload upon chemical reduction and retarded release upon oxidation. In a second step, we embedded the nanocapsules into nanofibers by colloid-electrospinning, yielding a hierarchical composite structure. Remarkably, the encapsulation of the nanocapsules in the fibers provides two decisive advantages that are a higher selectivity of the release and a higher control over the release rate of payloads, which make them promising candidates for the application of anticorrosive self-healing coatings.

The use of lithium-ion batteries in demanding applications, such as in electric vehicles and grid level energy storage, has fueled research on new high-capacity electrode materials. Upon cycling, however, high-capacity electrodes such as Si undergo enormous volume expansion and contraction, which results in deterioration of electrical interfaces between Si particles and polymer binders in composite electrodes, destruction of the conductive network, and rapid loss of capacity. Here, we consider a self-healing approach to increase cycle lifetimes and reliability through restoration of the electrical interfaces. Self-healing Si composite anodes are achieved through dynamic ionic bonding at the interface between Si nanoparticles and the polymeric binder. Amino groups are covalently attached to Si nanoparticle surfaces. During anode fabrication, the ionic bonds are readily formed between the amine groups on Si particle surfaces and the carboxyl groups on poly(acrylic acid) binder, as confirmed by X-ray photoelectron and Raman spectroscopy. The dynamic ionic bonds can effectively manage the large volume change of Si anodes during lithium intercalation and heal the damaged electrical interfaces in Si anodes via reversible bond dissociation and reformation, leading to excellent cycling stability. We achieve Si composite anodes with a cycle life of 400 cycles and 80% capacity retention at a current density of 2.1 mA/g.

Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is a semi-conducting polymer blend frequently used as anode in solution-processed organic light-emitting diodes (OLEDs) and organic solar cells (OSC). Typically, the PEDOT:PSS film is covered by at least one photoactive layer. These layers are typically thin (<100nm), and therefore prone to suffer from microscopic and macroscopic damage, leading to poor device performance due to low resistive contact between cathode and anode. Elevated damage risks are encountered in flexible devices, an example being rupture of printed metal tracks for interconnecting and voltage control. This paper presents a highly effective repair procedure that prevents the occurrence of such short circuits and leakage currents by local over-oxidation of PEDOT. During post-treatment of the active device stack with a water-borne oxidizer, PEDOT becomes locally oxidized in areas where it is exposed. A model comprising a combination of General Effective Medium (GEM) theory and rate law kinetics will be presented, describing how the PEDOT:PSS conductivity depends on treatment time and oxidizer concentration. Fitting this model against experimental data not only quantitatively provides suitable repair conditions, but also yields information on the nano-morphology of PEDOT:PSS. Next, the repair procedure itself will be highlighted, showing how both as-processed and deliberately defected OLEDs and OSCs obtain full recovery of operational characteristics and efficiency. The presentation may also include results on dendritic healing of printed metal tracks.

Mimicking biological systems and the parameters used to manipulate them in everyday life—heat, light and electric field—inspired us to design multi-responsive polymers. Multi-responsive polymers are of interest in technologies such as a drug delivery, membranes, and biosensors where the ability to dynamically interact with their surroundings is important. We have developed three classes of polymers to respond to temperature and degradation, temperature and light, and reduction and oxidation triggers. Integration of the different responsive molecular units into a single chain constructing a block or random copolymer does not guaranty the preservation of all the desired properties. The materials’ physical state, solubility and synthesis can work in unpredictable ways as will be discussed in this presentation.

Autonomous strategies are developed for timed release of chemical additives that counteract aging and degradation of Li-ion batteries. We successfully encapsulate the battery additive, vinylene carbonate (VC), which promotes beneficial interfacial reactions between the active materials in an electrode and the electrolyte. Typically, VC is incorporated in a battery when it is manufactured but is rapidly consumed during the initial charge and discharge cycles. In our approach, microcapsules containing VC are designed for controlled release of the additive into the electrolyte over time. The VC microcapsules are prepared by a solvent-exchange method that allows VC to diffuse through the microcapsule shell—wall at elevated temperature. The release of VC from the microcapsules into electrolyte is evaluated at the room temperature by taking aliquots from the electrolyte at fixed time intervals and measuring the VC concentration by NMR. Our current microcapsules rapidly release 60% of the VC core in the first 24 hours and then slowly release up to 78% of the initial core material for the next 20 days. From the release profile of the VC microcapsules in the electrolyte, the diffusion coefficient and permeability values are estimated based on Fick’s first law. Pouch cells with electrolyte containing either VC liquid or VC microcapsules, are fabricated and cycled at a rate of C/10. The VC concentration of the pouch cells with VC liquid decreased after 5 cycles, in contrast to the cells with VC microcapsules where VC concentration actually increased.
Towards the first developments of Self-Healing Robotics: thermo-reversible Diels-Alder polymer networks in compliant actuators

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This multidisciplinary research presents, for the first time, the innovative concept of implementing self-healing (SH) polymers in Soft Robotics, more specific in compliant actuators. The introduction of these materials will potentially reduce the over-dimensioning of current robotic systems, leading to lighter systems and eventually to more efficient designs. Compliant elements used in next generation soft robots can be constructed out of available SH-polymers, making them able to autonomously heal cuts and perforations caused by sharp objects in unstructured environments. In addition, the use of SH-materials will have a beneficial impact on the life span of robotic components, reducing the required maintenance drastically.

Through prototyping, a feasibility study was conducted, in which two entirely different compliant actuator types; a series elastic actuator (SEA) and a soft pneumatic actuator (SPA) were investigated, focusing on the implementation of a SH-mechanism [1, 2]. The SH-mechanism of both actuator types relies on dynamic covalent polymer network systems based on the reversible Diels-Alder (DA) reaction. Macromolecular damages in these non-autonomous DA-polymers can be healed in a couple of hours using relatively low temperatures (70-130 °C).

Firstly, a self-healing mechanical fuse (SH-MF) was developed [1], which can be inserted in an SEA. Whenever a damaging overload, potentially damaging one of the actuator components, occurs on the system, the fuse fractures sacrificially and can be self-healed afterwards. Using this principle, all components are protected and there is no need for large over-dimensioning. Secondly, to evaluate the potential of creating an SPA entirely out of SH-polymer material, a single soft pneumatic cell was built entirely out of the DA-polymers [2]. From this single-cell prototype it is straightforward to build the first SH-multi-cell SPA, one that can self-heal damages caused by sharp objects. For both prototypes, the mechanical properties of the actuator were recovered after the complete healing of macroscopic damages.

HYDROGELS

HYDRO 02 161 Self-healing nanostructured colloidal gelatin gels for bone regeneration

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By utilizing individually weak but collectively strong, and reversible interactions between colloidal particles, self-healing colloidal gels can be developed. This novel class of hydrogels has recently emerged as promising biomaterials for applications in tissue engineering and regeneration. Based on this approach, we recently developed a class of nanostructured colloidal gels composed of oppositely charged gelatin nanoparticles or oppositely charged gelatin and inorganic nanoparticles (e.g. calcium phosphate or silica nanoparticles). Due to the reversible feature of electrostatic interactions, these colloidal gels showed extraordinary capacity of self-healing, which allowed them to be used as injectables for biomedical applications.

HYDRO 03 129 Self-healing hydrogels based on non-covalent calcium-bisphosphonate interactions

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Conventional cross-linking strategies for hydrogels generally rely on the formation of covalent bonds. The irreversibility of these bonds renders these materials incapable of self-healing since these bonds cannot be restored after rupture. Therefore, alternative non-covalent crosslinking mechanisms are currently being explored to allow for self-healing. Herein, we have investigated if hydrogels can be rendered self-healing by i) grafting calcium-binding bisphosphonate groups onto the hydrophilic polymers and ii) mixing these bisphosphonate-functionalized polymers with either soluble calcium ions or calcium phosphate (CaP) nanoparticles.

To this end, amino-bisphosphonate alendronate was covalently linked to i) star-shaped poly (ethylene glycol) (PEG) functionalized with amine-reactive N-hydroxysuccinimide esters, while amino-bisphosphonate pamidronate was linked to hyaluronan via thiol–ene photocopolymerization between acrylated pamidronate and thiol-modified hyaluronan. The degree of modification was followed by proton NMR. The final bisphosphonate concentration was quantified by ICP-OES. CaP nanoparticles were prepared using a wet-chemical neutralization reaction between calcium hydroxide and phosphoric acid. Bisphosphonated polymers were mixed with CaP nanoparticles or calcium chloride solutions at various absolute and relative concentrations. Self-healing properties were studied upon repeated gel network destruction using visual inspection and oscillatory rheology.

Physically cross-linked hybrid nanocomposite formed by mixing hyaluronan-bisphosphonate with CaP nanoparticles. The hybrid materials displayed rapid (within 5 secs) and pronounced (98%) self-healing behavior as opposed to poor and slow self-healing observed for covalently cross-linked and/or bisphosphonate-free control formulations (Fig. 1A). Mixing of hyaluronan-bisphosphonate with calcium chloride solutions did not induce gelation. Bisphosphonated PEG macromers, on the other hand, formed gels with considerable self-healing capacity upon mixing with calcium chloride solutions, but could not be cross-linked by CaP nanoparticles (Fig. 1B).

In conclusion, it was shown that hydrogels with strong self-healing capacity can be formed by exploiting reversible interactions between bisphosphonated hydrophilic polymers and calcium ions as present in solution (for PEG gels) or CaP nanoparticles.
HYDR 04 29 Designing Extremely Resilient and Tough Hydrogels via Delayed Dissipation
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While high resilience of a material requires low mechanical dissipation of the material under deformation, high toughness requires significant mechanical dissipation during crack propagation. Here we reconcile this pair of seemingly contradictory properties to design extremely tough and resilient hydrogels. We propose a resilient domain for hydrogels’ deformation, below which hydrogels are deformed with low mechanical dissipation, but above which the deformation is highly dissipative. Therefore, hydrogels will appear resilient under moderate deformation within the resilient domain, but materials around crack tips will be deformed beyond the resilient domain and thus dissipate significantly to toughen the hydrogels. We implement the resilient domain by pre-stretching an interpenetrating-network hydrogel to damage the short-chain network to a controlled degree. The resultant hydrogel is highly resilient if deformed within the pre-stretched range (i.e., resilient domain), but highly dissipative if deformed beyond the resilient domain because of further damage of the short-chain network – achieving both high resilience of 95% and high toughness of 1900 J/m². To quantitatively explain the experimental results, we further adopt an interpenetrating-network model with network alteration, which can guide the design of future resilient and tough hydrogels.

HYDR 05 149 Formation of Self-Healing Colloidal Gels based on pH-induced Self-Assembly of Gelatin and Silica Nanoparticles
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PROJECT GOAL:
Natural materials such as bone exhibit unique self-healing properties owing to individually weak but collectively strong, as well as reversible, interactions between organic and inorganic phases. Colloidal gels - defined as continuous networks of aggregated particles - can also form owing to reversible, non-covalent interparticle interactions, resulting into considerable recovery of their mechanical properties after gel network destruction. Herein, we have investigated if organic-inorganic colloidal gels formed by pH-induced self-assembly of amphoteric gelatin and negatively charged silica nanoparticles also display self-healing properties.

APPROACH:
At high pH, both types of nanoparticles were negatively charged, repelled each other and therefore could be uniformly mixed. A controlled reduction of pH was achieved through time-dependent decomposition of glucono-d-lactone (GDL), which led to the charge reversal of gelatin nanoparticles. The formation process of colloidal gels as well as their structure was visualized by confocal fluorescence microscopy. Furthermore, the viscoelastic and self-healing properties of the gels were evaluated by rheological measurements.

RESULTS:
Confocal fluorescence microscopy demonstrated the in-situ self-assembly of the nanoparticles and the process of colloidal gel network formation. It was observed that the gel network structure and stability varies by changing the silica/gelatin mixing ratio (R). Generally, by increasing R, the thickness of gel network strands and the stability of gel networks increased. These results were supported by the rheological measurements. Moreover, the gels with R=5 showed high degrees of self-healing and could significantly recover viscoelastic properties after the gel network destruction to values that even exceeded the original gel elasticity (Figure 1).

CONCLUSIONS:
In summary, self-healing colloidal gels were formed by pH-induced self-assembly of gelatin and silica nanoparticles. The gel network structure and properties could be modulated by tailoring the preparation parameters such as the mixing ratio and pH condition. Specific gel compositions exhibited high self-healing abilities exceeding 100%.

MATERIALS CHARACTERIZATION

CHAR 01 98 A nonlinear fracture mechanics approach to the assessment of the interfacial healing in self-healing elastomers
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Several chemical routes are currently explored to create elastomers with self-healing functionalities at room temperature via the inclusion of hydrogen bonding, disulfide bridges, ionomers or other reversible chemical bonds. Despite these advances in the material development there are no generally accepted methods for the evaluation of the healing efficiency while most researchers only use some form of tensile testing. In the present work a fracture mechanics testing procedure, based on the application of the J-integral methodology, is proposed to investigate and quantify the self-healing behaviour of healable elastomers based on different chemistries. The new fracture mechanics approach is compared to traditionally-used tensile testing. Our research indicates that the standard tensile and fracture experiments probe different aspects of the healing mechanism. The processes involved in the repair can then be identified by combining the information obtained with the different techniques achieving a substantial improvement in the assessment of the interfacial healing as well as the mechanism of healing. These results also highlight the need of defining "healing efficiency" as function of the testing conditions.

CHAR 02 175 Neutron Scattering Investigation of a Covalent/Non-Covalent Self-Healing Polymer
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Recently, the first self-healing thermoster elastomer on the basis of poly(urea-urethane), reversibly cured with aromatic disulfide bridges, which requires no intervention to induce its repair, was reported. Here, a microscopic investigation by means of small angle neutron scattering (SANS) under uniaxial deformation before and after healing is performed. For this, a deuterated mesh as the label was built in chemically and its response on the molecular level to the applied deformation coupled to the mechanical characterization of the self-healed rubber at different stages. As the self-healing aspect of this thermoster is directly connected with the combination of two different dynamic bonds, i.e. a covalent disulfide linkage and a non-covalent hydrogen bond, each with different strength, the SANS evaluations aim at the understanding and the decomposition of both mechanisms. The work is performed within the framework of a FP7 funded project on Self-Healing-Innovative-Elastomers (SHINE).
Self-healing in cementitious materials is rooted in a combination of physical (e.g., transport properties) and chemical processes (e.g., precipitation of chemical compounds and additional hydration). This study adopts Raman spectroscopy coupled with x-ray computed microtomography to understand the evolution of the healing process, as well as the chemical composition and distribution of self-healing products within cracks. The results show that the self-healing mechanism is strongly influenced by the chemical composition, crack width or geometry of the cementitious material, and environmental exposure conditions. The resulting self-healing products vary, exhibiting different physical and chemical properties. The results from this study can help answer fundamental questions such as what is the dominating self-healing mechanism within a crack, how do self-healing products grow, and if the self-healing process can be controlled to design new and robust self-healing cementitious materials.

Research in the field of smart materials that exhibit self-repair mechanisms has greatly expanded over the last few years. This is especially true for polymers and polymer composite materials. One class of self-healing polymer materials is the reversible covalent polymer network system that uses dynamic covalent bonds as a means to repair sustained damage. Currently a range of different dynamic covalent bonds is considered, of which the reversible Diels-Alder chemistry has drawn the most attention. Reversible covalent bonds have been incorporated into polymer network structures based on the thermoreversible Diels-Alder reaction between a furan and a maleimide and by means of the photo reversible Anthracene dimerization reaction. Repair of sustained damage can be established by different healing actions in bulk materials as well as in coating applications using the appropriate stimuli.

The aim of this research is to study the healing mechanisms and healing kinetics at the microscopic scale and to compare these healing mechanisms for different polymer network structures and chemistries. The self-healing behavior is studied using local and surface analysis techniques, including Atomic Force Microscopy. A thorough evaluation of the healing mechanisms at the microscopic level will lead to a better understanding of macroscopic healing phenomena and ultimately to adapt the polymer network structure to obtain the desired material characteristics, such as healing conditions, mechanical properties and additional functional properties desired for various applications and healing procedures.

Loss of mechanical properties of bituminous materials may result from several different failure mechanisms. One of the most important is failure initiated by micro-cracks which, if not repaired, form macro-cracks. However, by momentarily reducing the viscosity of bitumen, it is demonstrated that bituminous materials can recover mechanical properties. If the material temperature is increased up to a temperature between 50°C and 100°C (depending on the type of bitumen), the bitumen starts flowing. Eventually, considering an opening-mode crack as defined in fracture mechanics, bitumen finds room to flow into the crack filling it up gradually. After cooling down, the healed material becomes more resistant. To stimulate the healing of micro-cracks within bituminous materials, one can use an alternating magnetic field as a trigger to generate heat.

We propose in this study to use magneto-responsive particles with tunable thermal response allowing an optimal strategy to close micro-cracks. Thermal responses of the particles in bituminous materials are studied experimentally and theoretically. It is found that by adapting the field conditions or the particle volume ratio, heating time can be reduced. If not well-monitored, local high temperatures may damage irreversibly the bitumen properties. To understand the physical, rheological and chemical changes with temperature, we investigate the microstructural behaviour of the bitumen surrounded by a magneto-responsive particle. Investigations at micro-scale are carried out to determine the conditions and the limits for promoting fast and homogeneous crack healing in a asphalt using Atomic Force Microscopy (AFM), Dynamic Shear Rheometer (DSR) and Fourier Transform Infrared Spectroscopy. The changes observed are function of thermal history (including repeating cycles), composition and types of particles.
MECANOCHEMISTRY

MECH 01 230 Mechanoochemistry in Glassy Polymers: Experiments and Simulations on Spiropyran-linked Poly(methyl methacrylate) 
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Polymer multifunctionality can be designed through the incorporation of chemical groups termed “mechanophores” which have a specific chemical transformation in response to applied force. Understanding the role of external factors such as temperature, loading mode, and loading rate on the behavior of mechanophore-linked polymers is critical for practical application of these polymers, particularly for damage detection.

Here, we use spiropyran (SP) covalently bonded into lightly crosslinked poly(methyl methacrylate) (PMMA) in order to quantify the influence of these externally imposed factors. SP is a mechanophore that has a distinct color and fluorescence change when activated through force to the merocyanine state, making it ideal for in-situ studies. We monitor and analyze the full field fluorescence of SP-PMMA samples during mechanical loading under tension and compression, over 3 decades of strain rate, and over a 60°C temperature range. The typical SP mechanooactivation response exhibits three distinct regimes: minimal change through yield, followed by rapid intensity increase, and approach to a steady state. Stress strongly influences the rate of SP transformation, where stress increase by temperature decrease or strain rate increase substantially raises the SP transformation rate.

We then use this data to evaluate and adapt our constitutive model for the mechanoochemical response mechanophore-linked glassy polymers. This continuum model predicts mechanophore response based on mechanophore kinetics derived from density functional theory calculations and force transmission to the mechanophores from molecular dynamics simulations. Previously this model was validated with respect to room temperature shear experiments. The new dataset confirms prior predictions that mechanophores will react under bulk polymer compression and validates the choice of deviatoric stress magnitude as the driving force for mechanophore transformation. Conversely, the elevated temperature portions of the dataset highlight deficiencies in the original model, suggesting a revision to the restrictions imposed by the glassy matrix on the mechanophore kinetics.

MECH 02 242 Mechanochromism of Diarylbibenzofuranone-based Dynamic Covalent Polymers
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Mechanochemical polymers, which change their color in response to mechanical stress, have attracted much attention and experienced significant progress in recent years. A strategy for building mechanochromic polymers is to incorporate mechanically sensitive units into polymer chains. Diarylbibenzofuranone (DABBF) mechanically undergoes bond dissociation to corresponding radicals, which show blue color (Figure 1). It is known that greatest stress is applied to the center of polymers under external force. In order to efficiently transfer external stress from DABBF and to precisely investigate mechanochromic behavior of DABBF in polymers, we synthesized linear and star polymers with DABBF functionality via atom transfer radical polymerization (ATRP) and subsequent click reactions. Their mechanochromism was evaluated by grinding test and electron paramagnetic resonance (EPR) spectroscopy.

Linear and star polystyrenes with DABBF functionality in the center of polymer structures were synthesized by the click reaction of polystyrene with azide end functionality (Mn = 11600, Mw/Mn = 1.14) prepared via ATRP and either DABBF-dialkyne derivative or DABBF-tetraalkyne derivative. The Mn (Mw/Mn) of the obtained linear and star polymers were characterized to be 23600 (1.08) and 39100 (1.05), respectively.

Both of linear and star polymers showed rapid and remarkable color changes by grinding. Through EPR measurement, we found that the ratio of the generated radicals was much higher than that in DABBF monomer. These results indicated that grinding force efficiently transferred to DABBF units in the center of polymer structures.

MECH 03 57 Mechnochemical pyramidalization of alkynes
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The activation of chemical bonds using mechanical force, mechanochrome, is a key mechanism in the development of materials with intrinsic self-healing capabilities. Chemical bond scission events typically occur in materials under high stress, creating high-energy chemical groups that can be used to achieve self-healing. However, significant stress is required to accomplish a significant amount of covalent bond scission events. The development of mechanophores that are activated at lower stress levels could lead to self-healing triggering at earlier damage states.

A chemical solution to this problem is to create high-energy species before bond scission occurs. Pyramidalization of π bonds occurs at lower energies than bond scission, leading to a reduction in π* energy, i.e., making the atoms electrophilic. To test this hypothesis, we prepared polymers with chain-centered alkynes. During solvodynamic-induced unfolding, the force-vector is unaligned with the triple bond, leading to temporary trans-bending of the bond. When unfolding is carried out in the presence of nucleophiles, bond-forming events are observed. Significantly, mechanoochemical reactions are observed at molecular weights below 30 kDa, which is the typical limiting molecular weight for bond-scission events, pointing to mechanoochemical reactions at lower stress levels.
MECH 04 212 Design of Mechanochemically Active Interfaces
Meenakshi Sundaram (mm2422@cornell.edu), Meredith Silberstein, Cornell University, NY USA

Polymer interfaces are crucial to the functionality of polymer composites, adhesives, and coatings. Interfacial failure leads to extensive civil infrastructural costs and one possible strategy to reduce costs is to construct interfaces with autonomous healing and self-reporting capabilities. We focus on enabling such features by functionalizing the interface with force triggered chemical units called mechanophores. For self-reporting interfaces a potential mechanophore transformation would be becoming fluorescent; for autonomous healing interfaces a potential mechanophore transformation would be catalyst releasing. Relative motion at the interface will activate the mechanophore chemical transformation.

To identify factors that affect mechanophore activation at an interface, we build an idealized molecular dynamics and analytical model. The mechanophore is represented by two particles bonded together and governed by a double-well potential. The potential represents a reaction where the bond length between the two particles change. We subject the interfaces to shear and examine the effect of surface roughness, strain rate, strength of van der Waals interaction, and mechanophore to substrate attachment.

The results of our simulations demonstrate the significance of the mechanophore-substrate van der Waals interaction. By increasing the magnitude of this interaction we can increase the percentage of mechanophores activated as shown in the figure. Also, in comparison to a rough substrate a flat one triggers mechanophore activation for smaller relative displacements of the interface --- a consequence of stronger collective van der Waals interaction. In addition to this we will present the effects of mechanophore attachment and strain rates on activation.

MECH 05 46 Development of latent mechanocatalyst for copper(I)-catalyzed azide/alkyne “click” reactions
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In the recent years self-healing materials came more and more into focus of scientific research. During this time a large diversity of different healing concepts were developed varying in self-healing chemistry, but also in the methods of triggering the desired healing reaction. An auspicious concept for triggering self-healing is based on latent mechanocatalysts, which are activated by mechanical force only and thus ultimately just due to the damage event itself.[1]

We design a latent polymeric copper(I) catalyst, which can be activated by mechanical force. For this purpose, we synthesized a bis(N-methylimidazolium-telecyclicP1B) copper(I) catalyst (see Figure 1), which is inactive in its initial state for copper(I)-catalyzed alknye/azide cycloaddition (CuAAC) reactions and after applying ultrasound within several cycles, mechanocatalytic activation could be obtained. Therefore, a model "click" reaction of benzyl azide and phenyl acetylene was chosen in order to evaluate the activation behavior with respect to molecular weight, solvent as well as applied ultrasound power. Good conversions for higher molecular weight catalysts are proven by 1H-NMR spectroscopic investigations. An application of such catalysts within azide and alkyne containing matrix material reveal a suitable approach for autonomous self-healing materials.[2-4]

MICROCAPSULES

MCAP-POLY 01 34 Recovery of mechanical and electrical properties in conductive self-healing polymer composite coatings
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Electrically conductive epoxies are often used as external coatings or 'bulk' packaging materials for electronic devices and are as such prone to cracking. Cracking results in loss of electrical conductivity and permeation of aggressive environmental elements into the device leading to a reduction in or loss of function. The goal of this research is the fabrication and evaluation of coatings based on an electrically conductive epoxy possessing the ability to autonomously restore barrier, mechanical, and electrical properties upon the formation of a crack via a microcapsule-based self-healing mechanism. For this purpose, microcapsules containing ethyl phenyl acetate (EPA) and carbon nanotube (CNT) filled epoxy resin were synthesized and incorporated into an electrically conductive coating. Upon crack propagation, the microcapsules are opened and the core materials released. EPA swells the epoxy matrix and (with the help of the CNT filled epoxy) facilitates the encounter of the two crack planes resulting in interface healing. Two different self-healing coatings and two controls based on an electrically conductive epoxy resin containing CNT's were fabricated and two methods developed to assess the degree of self-healing of controlled cracks after 24 hours. Electrical Impedance Spectroscopy (EIS) was employed to evaluate the potential of the CNT and non-CNT containing encapsulated systems to restore barrier properties to aggressive substances. Also, the extent of mechanical and electrical conductivity restoration was measured via an in situ tensile loading and electrical conductivity test. EIS testing indicated the restoration of barrier properties when microcapsules containing both EPA and CNT filled epoxy were incorporated into the coating. The sealing of electrical conductivity after mechanical cracking and 24 hours rest time was approximately 60% (± 23) while that of the stiffness was 81% (± 39). Also noteworthy, the tensile-electrical test was capable of detecting multiple damage-heal events in terms of electrical conductivity.

MCAP-POLY 02 88 pH-Dependent Switchable Permeability from Core-Shell Microcapsules
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Core-shell encapsulation is frequently limited by the degree of tunability of the system, which is usually addressed by adding unnecessary complexity in the form of composite systems. However, to address these limitations, we recently reported cationic cyclopolymerization of o-vinylbenzaldehydes initiated by boron trifluoride to generate acid-sensitive poly(o-(α-alkyl)vinylbenzaldehyde). Herein we describe preparation of core-shell microcapsules (µCs) using flow-focusing microfluidic techniques with shells composed of poly(o-(α-methyl)vinylbenzaldehyde) (PMVB) that release their payload in response to dilute aqueous acid solution. Release profiles of encapsulated fluorescein isothiocyanate-labeled dextran from µCs are controlled by varying the proton concentration and shell-wall thickness. SEM and Nanoindentation studies indicate the system’s unique reversible release mechanism involves porosity and chemical changes in the shell wall due to micro-crack formation, and we will discuss some of the ongoing applications.
Capsule-based self-healing approaches depend critically on microcapsules that possess shell walls with excellent barrier properties to achieve long shelf life. A substantial amount of work has been documented to correlate with diffusive mass loss of encapsulated healing agent fluid. Double shell walled polyurea/poly(urea-resorcinol-formaldehyde) (PU/PURF) microcapsules that possess improved thermal stability in comparison to single walled PURF microcapsules offer a route to improved retention of healing performance over time. In this study, we investigate a rapid screening method to identify alternate double shell walled microcapsule chemistries to improve the barrier properties. Previous work has used aromatic polyisocyanates (Desmodur L75) and isocyanate prepolymer (Imthane PHP-80D) that contain a much lower NCO wt% as compared to polymeric MDI (methylene diphenyl disocyanate). In this research, the inner polyurea shell wall is polymerized in situ using varying functionalities of polymeric MDIs to study the effect of the higher NCO wt% on the barrier properties of the shell wall. Single layer PURF and double layer PU/PURF films are fabricated to mimic the shell wall structure of single and double walled microcapsules, respectively. Permeability cup testing (ASTM E 96) is conducted on these films as a rapidly screening to quantify the improvement in barrier properties of double walled microcapsules. The mass loss of a select group of amines, epoxies and organic solvents commonly utilized in self-healing applications are investigated. These results are then correlated with Thermo-Gravimetric Analysis (TGA) mass loss curves and with the self-healing performance of double walled capsules with the same chemistries.

Self-healing composites are materials that autonomously respond to damage in order to effect the restoration of a degraded property. The microcapsule-based self-healing approach embeds microencapsulated healing fluid(s) within a polymer matrix. These capsules rupture upon damage and initiate healing either by polymerization or mobilization of residual functionality. However, the finite fluid contents contained within microcapsules limits the characteristic damage size that can be healed. In this work, we investigate the solvent-induced actuation and self-healing of shape memory polymers (SMP). The shape memory effect is activated by damage-induced release of microencapsulated solvent and serves to close and compress the fracture surfaces. The solvent then mechanically bonds the damaged area via polymer entanglement. This synergistic close-then-heal approach enables healing of damage volumes larger than possible with non-SMP based systems. Potential solvent compositions were screened using Hansen Solubility Parameters to identify multiple solvents suitable for activation of specific SMP materials. The effect of solvent on the SMP glass transition temperature was experimentally quantified by differential scanning calorimetry. Ex situ application of solvent is successfully shown to close and heal cuts. In situ (i.e., capsule-based) healing is quantified by tensile testing to determine the potential healing efficiency of the system.

The scanning electron microscope (SEM) reveals the surface topology of a lotus leaf. It is structured with micro-papillae and nano-cilia covered with wax and exhibits superhydrophobic water repellency, resulted in self-cleaning. For the technical analogue of lotus leaf, we present a mimicking surface sprayed with the nanostructured microcapsules encapsulating mineral oil. Also, self-healing has been examined by measuring contact angle after releasing the oil out when the surface is ruptured. A microfluidic device with two successive cross-channels is prepared to obtain the double-layered droplets. The mineral oil was introduced into the center inlet of the first cross-channel with 5 μl/min and 1wt% PVA solution into two side inlets with 10 μl/min. The CH2Cl2 containing PS-b-PMAA was injected into two side inlets of the second cross-channel with 30 μl/min. The double-layered droplets of O/W/O were generated. They were collected and dried. Figure 1(b) shows the SEM of the oil-encapsulating microcapsules in the range of 20-40 μm sizes. To form nano-cilia on the microcapsule, polyaniline was coated. The microcapsules were immersed in an aqueous solution containing 1 M HClO4, 6.7 mM ammonium persulfate and 10 mM aniline monomer at 0-4°C for 12 hours. Then, they were washed to remove the residual polymers. The nanostructured microcapsules were sprayed on the glass surface and the contact angle was compared to examine self-cleaning performance.

Self-healing composite materials possess the ability to respond to a variety of damage modes without human intervention. Although there has been remarkable progress over the past decade, incorporation of self-healing functionality in fiber-reinforced polymer composites continues to present challenges. In microcapsule-based self-healing approaches, many of the established healing chemistries suffer from a loss of reactivity after high temperature exposure, thus limiting material selection and manufacturing techniques. In prior literature, successful crack healing has been achieved in high temperature cured composites by incorporation of a thermoplastic phase in the matrix, but the application of heat was required. In this work, a thermoplastic (poly(bisphenol A-co-epichlorohydrin), PBAE) is blended with an epoxy matrix to simultaneously toughen and act as a healing agent in combination with an encapsulated solvent, ethyl phenyl acetate. Self-healing is assessed by incorporating microcapsules into tapered double cantilever beam specimens. A coating technique was employed to improve microcapsule thermal stability and the effect of the cure cycle on the microcapsules was evaluated. In situ healing is achieved with up to 57% recovery of fracture toughness in a toughened epoxy cured at 180°C, a common processing temperature for commercial composites. Additionally, the effect of increasing PBAE content on healing efficiency, virgin fracture toughness, glass transition temperature, and storage modulus was quantified. The material was also aged up to 30 days and demonstrated stable virgin fracture toughness as well as healing efficiency.
Self-healing materials offer the potential of changing the way engineers and designers think about polymers and composites in structural applications. These materials mimic biological materials by possessing the ability to react to damage by initiating a healing mechanism. One of the most successful approaches is to embed a microencapsulated adhesive in the polymer. However, while the mechanical properties of capsule-based self-healing materials have been thoroughly characterized, the thermal properties of these materials have not yet been as deeply studied. Here we present the results of a dynamic mechanical analysis of the thermal properties of a thermoset polymer matrix with embedded microcapsules as a model self-healing composite material. The glass transition temperature (Tg) was measured as heating rate, frequency, and weight percent microcapsules were varied. Tg was found to be directly proportional to the total weight percent microcapsules in the system. Neat samples exhibited a Tg of 115±3°C and there was a 2.1°C decrease in Tg per weight percent capsules added. In addition to the glass transition temperature, the creep performance of the microcapsule-epoxy composite was also studied.

Recently, self-healing polymers have attracted increasing interests, but most of the research concerns are focused on the extent of properties recovery rather than the speed. In fact, rapid healing of cracks is highly desired. On the one hand, crack propagates very fast; on the other hand, the damaged materials should be healed immediately to prevent occurrence of catastrophic failure. To tackle the problem, SbF5 and trifluoromethanesulfonic acid were employed for formulating fast healing systems in our lab, respectively. In actual operation, the acids were encapsulated by silica, and then embedded in epoxy matrix together with encapsulated epoxy monomer. Upon cracking of the composite, the fluidic chemicals released from the broken microcapsules flowed to the damage sites due to capillary effect and curing of the epoxy monomer occurred, re-connecting the cracked faces. Both impact and fatigue tests demonstrated that mechanical strength of the epoxy filled with the healing agent can be recovered within seconds at room temperature without manual intervention. Moreover, the healing system consisting of trifluoromethanesulfonic acid-epoxy pair turned out to possess significant thermal stability. It can survive the rigorous processing of high Tg epoxy (>240 °C) during composite fabrication and provide the composite that was pre-treated at 180 °C for 5 h with the same healing efficiency as the untreated one. We believe that the significantly improved self-healing speed and heat-resistance would help to move the smart functionality closer to practical application.

Polymeric thermostos, composites and coatings are susceptible to damages over time reducing the mechanical properties of these materials. This drastically affects many application fields such as construction, automotive and aerospace, industrial applications, wind energy, marine applications, etc. For this reason, the development of self-healing materials has become a rapidly emerging field over the last decade. Microcapsules embedded in the polymer matrix provide a promising technique for self-healing as they can rupture when a crack is formed in the material and release the encapsulated healing agent to repair the affected region by going through chemical reactions. However, the development of new synthetic techniques for the preparation of microcapsules as well as the optimization of existing processes is often performed via a trial-and-error approach. This often results in a time consuming and error-prone process. To overcome this limitation, we have developed a unique high-throughput platform for the synthesis of microcapsules with melamine-formaldehyde shell and cyclohexane as the core, which mimics the manual synthesis procedure very well, but speeding up the overall process using automated synthesis modules. These microcapsules were fully characterized and the influences of surfactant type and amount, core/shell ratio and shear rate on the formation and on the properties of the microcapsules were analyzed by varying the parameters over a wide range.

Over the last thirty years composite materials, plastics and ceramics have grown steadily, penetrating and changing markets relentlessly but also creating new opportunities. Nowadays composite materials represent a significant proportion of the engineered material markets ranging from everyday products to high-end niche applications. One of the successful strategies to deliver advanced composites is to develop stimuli responsive additives that are integrated into existing commodity products to deliver new and/or previously unmet performances. Devan chemicals is an SME that develops specialty chemicals for textile industry. This European sector suffered from globalization and the remaining companies are sustaining by developing high added value products. In this context Devan, with an open innovation mindset, is currently working on the development of microcapsules as additives. As successful examples phase changing microcapsules are currently sold in the bedding industry and microcapsules loaded with highly reactive components are under development for Self-healing composites. We will demonstrate that step by step moving from a vision to an attitude and finally to action, working microcapsules prototypes can be developed and integrated to deliver new advanced products.
This study presents a sophisticated monitoring system evaluating healing on both concrete and plastic. Recently developed smart materials autonomously repair damage by embedding dual-microcapsules (in thermosets) and macro-tubular capsules (in concrete). Several experimental methods are combined providing a full-field monitoring system that enables sensing of the healing process. Thus, a new generation of smart healing systems is introduced. Experimental testing clarifies the conditions under which autonomous healing polymer cracks and heals under mode-I fracture. The Tapered Double Cantilever Beam design is critically reviewed. The limitations of this setting due to manual pre-crack tapping and unstable stick-slip fracture are presented. The study introduces corrections on the healing efficiency constitutive law and proposes an alternative testing protocol that accurately measures the healing efficiency of thermosets. In the case of concrete, the complex and multi-scale concrete fracture and repair is measured by building a fracture testing protocol that highlights the conditions under which repairing process activates and occurs. Unique (mode-I fracture controlled by pre-crack) and multiple (realistic crack patterns) damage are formed assessing the repairing potential. A step further, the sealing and repairing efficiency is measured on real-size concrete structures.


**MCAP-CEMT 02 80** Self-healing of cementitious composites using silica precursors as microcapsulated healing agents
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Several different healing agents and mechanisms have been put forward for use in autonomous healing of small cracks in cementitious composites. While the existing research on this topic focuses mainly on the use of polymeric materials as encapsulated healing agents, this study aims at assessing the efficiency of inorganic silica precursors as potential healing materials. Herein, polyurethane microcapsules were developed to envelop inorganic aqueous core. Colloidal silica Ludox 40™, an aqueous suspension of fine silica particles, was selected as the appropriate healing agent. The suspended silica particles can react with calcium hydroxide in the matrix to yield further hydration products (C-S-H gel) and fill any existing voids. Microcapsules were synthesised in situ through a one-step interfacial polymerisation process and were subsequently dispersed in fresh cement paste. Two different mass fractions, i.e. 1 and 5% microcapsules/cement ratios, were investigated to assess the effects on both mechanical properties and healing efficiency. The self-healing capacity was evaluated by crack healing ratio and permeability reduction. Thus, three-point loading tests were performed on cracked, healed cement paste specimens, coupled with acquisition of microscopic images and gas permeability tests. The healing products were isolated and characterised through SEM, TGA and XRD. Furthermore, different ages of onset of the initial cracking were selected to isolate the effect of early age cracks. The results indicated that the encapsulation of healing agent in polyurethane could be regarded as a promising method for realising self-healing of cementitious composites.

**MCAP-CEMT 03 44** Investigation of self-healing in cementitious materials with sulfoaluminate cement microcapsules using X-ray computed tomography
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The paper presents work toward to study a new family of self-healing cementitious materials with sulfoaluminate cement microcapsules. A novel kind of microcapsule with sulfoaluminate cement was synthesized successfully. The research applied X-ray computed tomography and image analysis techniques to non-destructively examine the internal microcapsules and microcracks of cement based materials in order to clarify the self-healing progress and self-healing effect on microstructure characteristics. In the paper, through real time pre-loading and X-ray CT test, the microcracks were produced and tested in situ. And then the variation of microcracks and the self-healing of microcracks after different healing time, including 0day, 21day, 42day and 60day, were test in situ and analyzed by X-ray CT and image analysis. The results show that the cementitious materials with sulphate aluminium microcapsules have a recovering effect of micro cracks and microstructure.

**MCAP-CEMT 04 197** Production of microcapsules for self-healing concrete using microfluidics
Liviva Souza (livdas2@cam.ac.uk), Antonis Kanellopoulos, Abir Al-Tabbaa, University of Cambridge, UK

Capsule based self-healing is an effective method to obtain in autonomic healing in concrete, releasing healing agent to seal cracks and in some cases, obtaining partial regain in mechanical properties. Currently, the production of microcapsules containing liquid healing agent is achieved via emulsification and interfacial polymerization, even though this method presents challenges associated with the reactive nature of the chosen core material. Thus, in this work we propose the use of a new technology to create microcapsules for self-healing concrete, based on the production of double emulsion template using microfluidic device. Due to the small dimensions of the device, fluids present a laminar flow and reduced reactivity, enabling encapsulation of cores, which currently create great challenges using the emulsification polymerization technique. Moreover, this methodology of synthesis uses non-toxic substances and maximizes the incorporation of all materials used in the process, decreasing the waste generation and therefore leading to a greener chemistry. The production of microcapsules is comprised of two steps: firstly, water-in-oil-in-water droplets are produced followed by photopolymerization of the middle oil phase creating a solid shell and resulting in the formation of capsules. The shell material is comprised of a mixture of poly(1,6-hexanediol diacylate) and poly(bisphenol A glicerolate) encapsulating an aqueous core, which can further be used as a carrier phase for the healing agent. The capsules were characterized by TGA, FTIR, SEM and permeability tests to assess the long term stability of the materials.
Microcapsule with a shell responsive to water soluble ions are expected to be applied in many self-healing materials. Among them, that sensitive to chloride ion is deemed to be an effective means to resolve the chloride-attack problem of rebar in concrete. In this article, several kinds of chloride-responsive microcapsules were presented to illustrate the distinct trigger principles: (1) precipitation of AgCl or PbCl2. AgCl or PbCl2 has very low Ksp value, the shell materials made up of Ag+ or Pb2+ will be decomposed to produce AgCl or PbCl2 precipitant, so the content can be released. The Ag+ or Pb2+ compounds are carboxylate (e.g. stearate, laurate, oleate, etc.), poly-carboxylate (e.g. PAA, alginate, etc.), PbSO4, coordination or chelates compound (i.e organic metal complex, such as MOFs); (2) dissolution of chloride coordination compounds, such as [CuCl4]2-, [PbCl4]2-. In this case, the wall materials are the indissoluble chlorides (e.g. CuCl2, PbCl2), or hydroxide (e.g. Pb(OH)2) (3) corrosion of metals. Many corroded is in sea water. The microcapsule shell by these metals or embedded these metals on the shell can be triggered by chloride ion. These materials are Al, Cu, Fe, etc. (4) changing permeability of the shell. Many complexes of polymer ligands can comprises the microcapsule’s shell. Their water-permeability of water can be changed by ionic strength or concentration of given ion (e.g. co-P(vinyl imidazole-vinyl acrylic acid)-Ag+).

MICROVASCULAR SYSTEMS

MVAS 01 277 Development of 3D Printed Vascular Networks for Repeated Healing Cycles
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In nature, the efficient transport of fluid through vascular networks is crucial in enabling a biological system to repair and remodel itself in response to damage. By including similar features into vascular networks in order to deliver healing agents from an external reservoir to a damage site, the autonomous, in-situ restoration of mechanical properties is possible, and hence an increase in the service lifetime and reliability of these materials may be realized.

To date, the ability to achieve multiple healing cycles in vascular self-healing systems is limited due to fracture of the network, which is necessary to release the healing agent and allow it to permeate through the damage area. As a result, network thrombosis occurs which restricts further passage of the fluid. To overcome this key drawback, we present a novel concept that exploits adhesive failure of an embedded porous thermoplastic network from the host matrix when a propagating crack reaches the external network wall. Consequently, the radial pores of the network are exposed and the healing agent is able to permeate through the damage site under pressure. As fracture of the network is not required, the future supply of healing agent is not restricted, thus allowing for repeated healing cycles.

In order to develop this concept, porous networks have been designed and manufactured via thermoplastic extrusion and embedded into a polymeric matrix. Through a combination of experimental characterization and the generation of a microfluidics model, the ideal network design has been investigated with consideration of the crack-vascule interaction and flow of healing agent. A strength assessment has confirmed that the healing agent is able to infiltrate the damage site without fracturing the network, leading to the possibility of future healing events. Further characterization of the self-healing delivery system, (the network material, geometry and printing parameters), together with the compatibility of the healing agent to maximize the restoration of the structural efficiency of the damage area, will be discussed at the conference.

MVAS 02 209 Restoration of Catastrophic Damage in Polymers
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The healing and regeneration of damaged tissue is common in biological systems. Although self-healing capabilities have been demonstrated in synthetic polymers with embedded microvascular networks, previous work was limited to small (microscopic) defects and cracks. Damage events that involve significant mass loss such as ballistic impact represent a technological challenge that has been unachievable to date. Liquid healing agents are susceptible to bleed-out due to forces imposed by surface tension and gravity.

Here we demonstrate the first synthetic system that regenerates in response to large-scale damage. Two-stage polymer chemistry provides a technique to mitigate bleed-out and restore system performance through the use of two distinct rheological transitions. Following in situ microvascular delivery, healing agents rapidly gel to aid in fluid retention and later transition into a robust, structural solid. By optimizing reaction kinetics, microvascular architecture, and delivery protocol, we achieve a maximum recoverable diameter of 11.2 mm for through-thickness cylindrical defects in thin epoxy sheets. Damage-triggered regeneration will lead to synthetic materials systems capable of vastly extended life, damage tolerance, and safety.

MVAS 03 202 Impact Puncture Restoration in Bulk Polymers
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While self-healing strategies have been successfully applied to repair damage at microscopic length scales such as scratches or cracks, the restoration of materials that suffer significant material loss such as impact puncture damage has remained an unmet challenge until White et al. introduced a 2-stage restorative chemistry and demonstrated its applicability to recovery both idealized cylindrical damage, as well as impact puncture damage. [1] This study aims to more fully characterized factors that influence the restoration of impact damage, and improve upon the restoration performance previously demonstrated. Results are presented summarizing the restoration performance of impact puncture damaged specimens, characterized by both pressure seal testing and recovery of absorbed impact energy. Bulk polymer specimens are damaged with a drop tower apparatus to produce a central puncture damage with radiating cracks and damage spanning ~35 mm in diameter. Impact damage is restored with the 2-stage chemistry, which exhibits two distinct and controllable transitions in mechanical properties: first from liquid to gel, and subsequently from gel to stiff polymer. Pressure seal testing is performed by applying a 345 kPa N2 to one side of the specimen and monitoring leakage on the opposite side. Recovery of absorbed impact energy after restoration is measured by re-impacting the restored specimens using the same impact testing protocol. Factors influencing restoration are explored first. Variations in the restoration chemistry are discussed: specifically the effect of gel time, mechanical properties, and chemical composition. Second, multiple configurations of the bulk substrate are tested: type of polymer, introduction of more complex vasculature, and inclusion of microcapsules. The restoration of large damage volumes is a developing field for self-healing materials, incorporation concepts from biological regeneration. Newly introduced 2-stage chemistry offers an avenue of research to address the multi-scale damage geometries. Challenges for impact damage restoration will be discussed as well as future directions to address damage in which large volumes of material are lost.
In biological systems, fluid transport through internal vasculature enables a plurality of metabolic and homeostatic functions including respiration, circulation, thermal regulation, and self-repair. Natural, load-bearing materials such as bone and wood rely on nutrient exchange through a series of complex networks to achieve mechanical stasis via cellular proliferation (growth) and tissue regeneration. While synthetic fiber-reinforced composites (FRC) attain comparable specific strength/stiffness properties to these living hierarchical materials, the ability to sustain structural performance over a wide range of environmental conditions and engineering applications has yet to be accomplished. One promising pathway for accession of multifunctionality in man-made FRC is to mimic successful, evolutionary-derived vascular constructions.

Here we show advancements for a recently developed technique [2-4] designated vaporization of sacrificial components (VaSC), where inverse replica microvasculature is created within fiber-composites through thermal depolymerization of a sacrificial precursor. Metal catalyst micro-particles are incorporated into a commodity biopolymer, poly(lactic) acid (PLA), and extruded into printable filament for an additive manufacturing process known as fused deposition modeling (FDM). The sacrificial printing technique is both economical and scalable using commercially available materials, processes, and equipment. By expanding the VaSC procedure beyond one-dimensional (1D) segregated channels, to three-dimensional (3D) interconnected networks closer resembling biological vasculature (Figure 1), the range of dynamic functionalities for fiber-composites is increased. In addition to providing enhanced multifunctional capabilities, 3D printed networks also possess damage-tolerant features found in natural vasculatures. This latest advancement of bioinspired vascular redundancy improves upon our prior approach [3] to achieve in situ self-healing of interlaminar delamination over multiple cycles.

Work into synthesizing microvascular materials has recently taken a step forward in the form of a new synthetic process VaSC (Vaporization of a Sacrificial Component) that enables the formation of 3D microstructures that are meters in length. We report on our recent advances in using VaSC to create three-dimensional gas exchange units modeled on the design of avian lungs and vascular systems for heat distribution. We are focused on using these materials and dynamic chemical reactions to remodel the material within the vascular structure. In this case, we seek to make materials that improve their function in response to selective pressures.

**MODELING AND NUMERICAL ANALYSIS**

**MODL-POLY 01 89 Mathematical models of skin wound healing: a guide to the development of synthetic polymer coatings.**

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The basic principle behind the development of self-healing materials is the local activation and mobilization of healing resources. This principle is shared with many of the healing processes observed in nature, and it is well captured from a modeling point of view in bone and wound healing. In this work we focus our attention on the healing processes in skin wounds and, in particular, we discuss the fundamental aspects and the latest developments in their modeling. Subsequently, we will try to bridge our modeling hypotheses to the structure and requirements of self-healing polymeric coatings.

Skin is the outer protection barrier of the body, structured in a multi-layered configuration, of a fibrous nature and pre-stressed. Its response to a wound proceeds through a coordinated sequence of actions controlled by both chemical and mechanical stimulus. During the course of wound healing, different length- and time-scales are coupled, going from the release or attachment of molecules at the cell surface, the cellular cycle of proliferation and differentiation, to the mechanical equilibrium of the tissue. Here we present a formulation of the healing process in terms of macroscopic variables, such as averaged cellular densities and chemical factors concentrations. The wound heals by the infiltration of one specific cellular species (fibroblasts) and its production of extracellular matrix. A closed feedback loop between the species and the tissue mechanical state is proposed, at the cellular level, through the combined action of the felt deformations and the proliferative chemical factors. Finally, the model predictive power is validated by comparison with reported experimental results (Valero et al., Plos One, Vol. 9(3):e92774, 2014).

**MODL-POLY 02 188 Modeling the fracture behavior of thermal barrier coatings in the presence of healing particles.**

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Thermal Barrier Coating (TBC) systems are applied on the external surface of critical structural components to protect them against melting and oxidation when exposed to high-temperature environments. However, under thermo-mechanical cyclic loading, micro-cracks nucleate and grow in the TBC system, which, upon failure, leaves the substrate unprotected. A typical TBC system consists of three different layers, namely a ceramic top coat (TC), a thermally grown oxide (TGO) layer and a metallic bond coat (BC). In the self-healing TBC system examined here dispersed healing particles are contained in the TC layer. For the design of a robust healing system, it is important to understand the failure behavior of the TBC. In particular, the depth at which cracks are likely to initiate need to be identified to judiciously distribute the healing particles. To achieve this, cohesive element-based finite element fracture analyses are conducted. Distinct fracture properties and microstructural features such as interface roughness and porosity are considered in the modeling as shown in Fig.1. Moreover, the interaction between cracks and healing particles are analyzed under thermal loading and assuming the healing particles to be dispersed in the TC close to the interface between the TC and TGO layers. Several configurations for the healing particles have been analyzed to assess the influence of the particle distribution. This study helps to identify the optimal configuration of the healing particles for successful activation of the healing mechanism.
Applying heat to polymer interfaces is a common means of welding polymer components or healing cracks in polymers. Once chains have diffused by their radius of gyration, the properties of the interface should be indistinguishable from those of the bulk. In practice, welds can achieve bulk strength at much shorter times. The mechanism of strength growth is difficult to determine with experiments, because they cannot directly access the evolution of molecular configurations and entanglements. Large-scale simulations were used to follow the dynamics of interdiffusion at welds and cracks and the associated changes in density and molecular conformations. The evolution of entanglements was tracked using Primitive Path Analysis and shown to be directly related to the mechanical strength under shear and tensile loading. As in experiment, the maximum shear strength emas of a homopolymer interface rises as a power of welding time and then saturates at the bulk value. Simulations show that emas is proportional to the area density of interfacial entanglements at short times and saturates when chains have formed 2-3 entanglements across the interface. Enthalpy limits interdiffusion across heteropolymer interfaces, and there is a corresponding reduction in interfacial entanglements and mechanical strength. A minimum loop length of order the entanglement length must diffuse across the interface to form entanglements. Cracks are more complicated because of the presence of short segments produced during fracture. Segments that are too strong to confer bulk strength, but longer than the entanglement length, remain near the interface for long time intervals. This leads to a plateau in strength that is below the bulk value. Crazes form under tensile loading. A low interfacial entanglement density can stabilize craze formation and significantly enhance the fracture energy, but the bulk fracture energy is recovered at about the same time as bulk shear strength.

The ability to sustain large-scale deformations, and subsequently recover shape and structure upon unloading, is a highly desirable property in composite materials. Cross-linked networks of polymer-grafted nanoparticles (PGNs) constitute a class of composites with tunable mechanical properties that exhibit such a self-healing behavior. A PGN network consists of nanoparticles that are decorated with end-grafted polymer chains. Reactive groups on the free ends of these grafted chains can form bonds with the chain ends on the nearby particles. We study these materials using a 3D multi-scale computational model that encompasses the particle-particle interactions, the kinetics of bond formation and rupture, and the external forces applied to the network. In our model, a fraction of cross-links is formed through biomimetic “catch” bonds. In contrast to conventional "slip" bonds, catch bonds can have a longer lifetime under an applied force; this behavior is due to force-induced transitions between two conformational states. Hence, the catch bonds effectively become stronger under a deformation. We show that the mechanical properties of PGN networks exhibit a dramatic improvement with the introduction of catch bonds. The simulations revealed that controlling the fraction of these catch bonds in the network, higher extensibility, improved toughness and faster strain recovery could be achieved in these composite materials.

The particle-based self-healing mechanism has received considerable attention for a range of materials and systems. In such systems, particles or capsules containing a healing agent are dispersed in a matrix material. Cracks present in the matrix interact with the healing particles and trigger a healing mechanism. Subsequently, the mechanical integrity of the material should be restored. For healing activation, a crack initiated in the matrix should open the healing particle instead of deflecting away from it (see fig. 1). Hence, the study aims at providing information regarding the mechanical properties of the particle relative to the matrix material, in terms of elastic stiffness, fracture strength and toughness, required for triggering the healing mechanism.

A matrix-single healing particle system is considered and fracture mechanics analyses employing cohesive elements have been performed in a finite element framework. Parametric analyses are carried out to study issues such as the effect of mismatch in elastic and fracture properties between the particle and the matrix. The effects of pre-existing flaws within the particle, which may occur during manufacturing, are also taken into account. Fracture maps are generated for different flaw configurations in terms of size and orientation, which distinguish the two fracture mechanisms, namely, particle fracture and crack deflection. The effect of interface properties has also been studied to establish the conditions under which a crack deflects along the interface or penetrates into the particle. The framework developed can be used as a tool to design and analyze various particle-based self-healing systems.

The paper describes a new thermohygro-chemical finite element model for simulating natural and enhanced self-healing transport processes in cementitious materials. The governing equations are derived from the mass balance equations for liquid water, vapour and healing solute, as well as the enthalpy balance equation for heat flow. The model assumes that all transport processes occur within the moisture phase of the capillary pore network and that the driving mechanisms for flow are the advective, diffusive and dispersive fluxes. The degree of saturation, and thereby the moisture content, is related to the driving capillary pressure via a modified van Genuchten isotherm. The dissolution and precipitation of the self-healing solute are approximated with a Freundlich type of isotherm. The finite element equations are fully coupled and are discretized using a Galerkin weighted residual in space and an implicit time stepping scheme in the temporal domain. The resulting nonlinear equations are solved using a Newton type solution algorithm. The work has explored healing in both early age and mature specimens. For the latter, the model of Schlinder and Folliaard [1] has been employed to simulate the heat and degree of hydration. The model has been applied to a set of experiments undertaken in Cardiff University that measured the transportation of 'healing products' in cracked early age and mature mortar specimens. In the former case, a chemical analysis showed that majority of the material transported to the crack was a mixture of unreacted cement and Portlandite, whereas in the latter long-term case, calcium carbonate was the dominant material. The numerical predictions demonstrated that the model is able to reproduce the essential characteristics of these experiments.
Cracks, caused by volume changes and mechanical loading, are an inherent feature of cementitious materials. Aggressive and deleterious substances penetrate into the concrete via these cracks, and may jeopardize the durability of structures built with cementitious materials. Interestingly, some old structures perform excellently, probably as a result of autogenous or self-healing of fine cracks. This self-healing is attributed to further hydration of unhydrated cement particles. The hydration products fill the fine cracks and can block the ingress of harmful substances.

Previous studies have shown that the formation of healing products in cracks indeed enhances the service life. Unfortunately, the effect of different parameters on self-healing is not clear yet. For example, cementitious materials casted using cements with different fineness have different microstructures. Different microstructures exhibit different crack patterns and different distribution of unhydrated cement grains, which are considered as key factors in self-healing of unhydrated cement and transport properties.

In this study, a numerical modeling procedure is proposed for predicting the effect of self-healing on the transport properties of concrete. The microstructure of cement paste is simulated by HYMPSTRUC3D. Then the cracks are created using a lattice fracture model. The ‘void’ elements, ‘solid’ elements, ‘cracked’ elements and ‘self-healed’ elements are supposed to have different water permeability coefficients. The effect of several parameters, like the cement fineness, the water-cement ratio, on the efficiency of self-healing and change of transport properties are investigated. Tentative conclusions will be drawn regarding the effect of cement fineness on the long-term performance of concrete structures.

Keywords: self-healing, fineness of cement, further hydration, durability, transport properties.
SUPRAMOLECULAR POLYMERS

SUPR 01 47 Relationship between the network relaxation time and supramolecular self-assembly time and the healing kinetics in ionomers
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Relaxations in polymers are related to molecular mobility, and these relaxations manifest themselves in the macroscopic mechanical behaviour of the polymers. These relaxations could be associated with the dynamic nature of the reversible interactions or could arise from the chain relaxations of the polymer backbone itself. The aim of this work is to study the relationship between molecular timescales and actual repair timescales.

The reversible polymers used in this work are a subset of supramolecular polymers known as ionomers, which have polar ionic groups that phase segregate into regions of restricted mobility known as clusters. Creep relaxation experiments were performed at different temperatures to determine terminal relaxation times. Frequency sweeps in oscillatory shear rheology were used to determine the dynamic reversible timescale. The temperature dependent timescales were used to calculate the Arrhenius type activation energy of the clusters and the flow of the polymer backbone. These timescales were compared to theoretical models for supramolecular networks in order to select the best model describing the phenomena taking place.

In order to relate the network and cluster relaxation times to macroscopic phenomena, self-healing tests were performed. For this two discs of the samples were heated past their ionic transition temperature and then brought into contact together for a certain amount of time at different temperatures. Upon applying a controlled strain to break them apart, the resulting force-displacement data showed that beyond an initial de-cluster activation, the chain rearrangement processes played a large role on the recovery of mechanical properties. We show that the kinetics of healing closely follow the network and cluster timescales.

SUPR 02 95 Interactions between Supramolecular Self-Healing polymers and Inorganic Reinforcements
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A critical issue when designing self-healing polymer matrix composites consists in the repair of damage that occur at matrix-fiber interfaces, such as delaminations and matrix-fiber de-bonding.

To this end, matrix materials that are able to form strong interactions with the reinforcements and to re-form bonds after an interface failure event would be of high interest.

In this perspective, we investigated the interactions between self-healing polymers and an inorganic phase, glass. The polymers are partially supramolecular materials [1]: their networks incorporate chemical and physical cross-links, the latter through cooperative hydrogen bonds. The physical cross-links are responsible for the final self-healing ability, and their proportion is tuned to tailor the final materials properties.

We considered the adhesion of the matrix towards a model substrate (glass), and its ability to recover adhesion strength after debonding. An adhesion test was developed, in which the polymeric material was cured between 2 glass substrates and the samples were tested in failwise tensile mode. After the test, they were put back together and tested again after a rest period.

The second investigation evaluated the ability of the polymers, once freshly damaged, to interact and form secondary bonds with glass reinforcements. The strength of the formed bonds was quantified by separating the polymer from the substrate in a tensile test.

We will report on the adhesion and recovered adhesion strength values for different self-healing polymer compositions towards glass, and analyze the results in function of the relative content of physical cross-links in their network and of different silylation of the glass substrates. The increase of physical cross-links content and the silane treatments of the glass are expected to increase the adhesion properties as well as their recovery.

SUPR 03 189 Polybutylene oxide model polymers with hydrogen bonds
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This contribution summarizes the synthesis of polybutylene oxides (PBO) functionalized with hydrogen bond forming groups. In addition the physical characterization of the materials using mainly rheological and scattering methods is described.

The aim of our work is to obtain an understanding of self-healing processes on a molecular level. For the physical studies precisely defined polymers are required. We have chosen PBO, which can be obtained via anionic ring opening polymerization as homopolymer equipped with terminal alcoholic groups. Alternatively the polymer can be synthesized with randomly distributed backbone functionalities using copolymerization processes. We will report the synthetic procedures to end- and backbone functionalize the polymers with hydrogen bond forming groups, especially the DAT-thymine and urazole systems. A detailed NMR based study will be presented which allows the precise determination of the functionalization degrees.

Besides narrow molecular weight distributions the polymers exhibit low Tg values of about -80 °C and reasonably low entanglement molecular weights of 8k. As a consequence the full relaxation time spectrum is obtained via dynamic mechanical analysis, complemented with dielectric spectroscopy. The moderately polar PBO suppresses non-directed interactions of the supramolecular moieties like clustering as confirmed in initial rheological experiments. Adding monofunctional arms to backbone functionalized material; transiently branched architectural polymers are obtained and are investigated with neutron scattering techniques.

SUPR 04 146 Self-healing via “click”-based concepts and supramolecular principles
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With the advent of SH materials a new vision of material science had been accomplished, together with the exploitation of chemical and physical principles [1]. Thus e.g. encapsulation has been optimized for embedding of reactive components [2] allowing sufficient fast crosslinking and crack-repair after mechnochemical damage [3]. The application of supramolecular bonds [4] acting as reversible crosslinking systems enables multiple SH principles [5] taking into account the relevant timescales of self-healing [6]. The current presentation addresses principles of self-healing polymers active via combined capsule based principles and supramolecular healing concepts. The combination of both healing principles promises to obtain multiple healing-cycles together with a mechanically stronger material. Issues addressed are the use of carbon-based nanofillers [7] bearing attached catalytic groups to enable “click”-based crosslinking in combination with supramolecular healing principles.
SUPR 05 111 A thermoreversible supramolecular polyurethane capable of highly efficient healing at 45 °C
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Ioannis Giannakopoulos, Xuegang Tang, Clive R. Sivour, C. Paul Buckley, Oxford University, UK

The development of healable polymers that are capable of repairing damage to surfaces or within the bulk material is an extremely attractive proposition within many industrial applications. To this end, materials able to heal in an autonomous fashion or via application of external stimuli such as heat, light or pressure have been generated. Several approaches to healable materials have been reported including irreversible covalent bond formation, utilization of reversible covalent bonds, release of encapsulated liquid monomers, or the employment of weak non-covalent interactions such as π−π stacking, hydrogen bonding or metal-ligand interactions.1

We have synthesized a supramolecular polyurethane whose mechanical properties can be completely recovered in 120 minutes by exposure to an elevated temperature of only 45 °C. This polyurethane is self-complementary; it uses a combination of hydrogen bonding and π−π stacking interactions to facilitate healing in contrast to previous studies in our group on complementary supramolecular polymer blends. 2 As a consequence of the molecular design of this polyurethane, we have achieved an elastomeric material which can be healed at easily accessible temperatures and thus it offers significant promise suitable for use in biomedical applications (i.e. surface coatings or adhesive formulations) or complex multi-component assemblies which will not withstand exposure to more intense heat treatments (Figure 1).

SUPR 06 55 Self-healing metallocopolymers: Investigation of the mechanism
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In the last fifteen years several strategies have been developed to design self-healing polymers. The intrinsic self-healing is based on the reversibility of a structural element. Therefore, several approaches were investigated, e.g., Diels-Alder reactions, hydrogen bonds or ionic interactions. Another possibility is the utilization of metal-ligand interactions, which can be tuned by utilization of different ligands and metal salts. Beside the metal ligand interaction most of the metal complexes are charged and, thus, ionic interactions are also possible. The terpyridine ligand was chosen as a reference ligand, because it is well-investigated in solution. The moiety was incorporated into a polymer and afterwards crosslinked by the addition of several metal salts. The self-healing behavior was studied in detail (Figure 1) and it could be demonstrated that the nature of the metal-ligand interaction has a high influence on the self-healing ability. In particular, the crosslinking with cadmium acetate leads to a system with two bridging acetate moieties that have a rather low binding constant with the cadmium metal center.

Thus, healing at temperatures as low as 70 °C is possible. Furthermore, the underlying mechanism was studied by different techniques. Therefore, Raman as well as SAXS measurements were performed. It could be demonstrated that a phase separation takes place resulting in the formation of ionic clusters. These clusters also contribute to the self-healing behavior of the metallocopolymers.

SUPR 07 196 New self-healing materials based on mixtures of poly(ionic liquids) and bromobutyl rubber
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In the last years, poly(ionic liquids) became an interesting field of material research due to the possibility to combine the favorable properties of ionic liquids and polymers, which opens a wide range of applications. Applications of these materials include absorption and separation processes, function as catalysts, use as polymer electrolytes, in fuel cells and as ion conductive material in batteries. [1] In addition, the strong ionic interactions of poly(ionic liquids) can be used for self-healing concepts. [2] Therefore, a two-step polymer-analogous reaction was performed to obtain new poly(ionic liquids) based on maleic anhydride-containing polymers (see Figure 1). In the first step, imidization of the maleic anhydride groups was performed with (1,3-aminopropyl)imidazole. The resulting polymer contains imidazole moieties, which were subsequently converted with different amounts of alkyl bromides. The variation of length and amount of these alkyl bromides allows tailoring of thermal behavior and solution properties. Also anion exchanges with different species were performed to influence the overall properties of the polymers e.g. glass transition temperatures and solution properties. The obtained poly(ionic liquids) were incorporated into blends of bromobutyl rubber. The ability to form reversible ionic clusters in the rubber matrix will be used to create self-healing behavior. Stress strain tests and mending test already showed indications of self-healing effects. Furthermore, the materials were characterized by different mechanical methods like dynamic mechanical analysis and curing behavior.

SUPR 08 36 A double self-healing system by combination of covalent crosslinking via the CuAAC click reaction
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Self-healing polymers are a major focus of materials scientists as a damage management concept [1]. In order to fully regain the original materials properties under ambient conditions, highly mobile and reactive multivalent polymers with different architectures and catalytic crosslinking reactions are applied.

Covalent crosslinking via click-reactions [2] ensures fast self-healing being restricted to a single self-healing event. In contrast, hydrogen-bonding motives enable multiple self-healing at a long lapse of time due to supramolecular interactions operating as a lock-and-key model. By combining covalent crosslinking via the copper(I)-catalyzed azide-alkyne click (CuAAC) reaction [3] with hydrogen-bonding interactions, a double self-healing system was realized, where multiple self-healing was achieved after covalent network formation.

We have designed four-arm star-shaped polymers bearing both, thymine moieties effecting supramolecular healing and azide-endgroups effecting covalent healing. Multiple self-healing of cut polymer films was demonstrated within 48 hours at room temperature, where the self-healing response is attributed to phase separation effects between the unpolymer backbone and thymine-endgroups via supramolecular cluster formation [4] resulting in tough rubbery materials with enhanced mechanical properties. [5]
The development of self-healing mechanisms that allow the repair of elastomers instantaneously on the molecular level is highly demanded in order to result in more reliable and durable elastomers. Ionomic materials that are crosslinked exclusively by dynamic bonds are recently shown to be of potential for autonomous or on-demand self-healing in flexible polymeric materials. In this respect, the use of ionomers represents a promising approach. The strong interaction between ionic moieties within a non-polar matrix leads to microphase separation in a thermally reversible network. The long lifetime of the ionic association and the temperature-reversible formation of ionic cross-links is an essential feature for the ability of intrinsic self-healing. The implementation and parameter optimization, however, requires a profound understanding of the structure-property relationships. For this purpose, we developed a model system for self-healing ionomic elastomers that allows a detailed insight into the interrelations of molecular structure, ion fraction, counter-ion nature, and the resulting mechanical and self-healing properties. Our results deliver a clear indication for the important impact of the inner structure of ionomer-based elastomers on their mechanical properties, both on their frequency-dependent, dynamic behavior as well as on their thermal characteristics, and that both parameters are essential for the self-healing ability and material reliability in these materials. The self-healing efficiency of the model ionomers is evaluated by tensile tests on macroscopically cut and healed samples. The damaged samples are healed under different thermal conditions and time ranges. The results clearly illustrate the principal potential of ionomers for the development of self-healing materials, and that an optimization of the self-healing effect with respect to the counter-ion nature and the ion fraction is possible.

**SUPR 09 205 Self-healing Processes in Ionomic Elastomers**
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Polymers with the ability to heal themselves could provide access to materials with extended lifetimes in a wide range of applications. Although a number of approaches to healable materials are known, (1) supramolecular polylayers are able to produce mendable materials that retain their mechanical properties over a number of break/heal cycles. (2) Here we describe a novel series of stimuli-responsive, π-stacked polymer blends comprising of π-electron-rich pyrenyl or perylenyl terminated polymers, which, when blended with a π-electron-deficient chain-folding polyimide afforded healable materials (Figure 1). (3) To improve the mechanical properties of healable π-stacked polymers, different degrees of supramolecular “cross-linking” were investigated. Divalent or trivalent polyether(s) featuring pyrenyl end-groups were blended with a known chain-folding polypdiimide(4) to form supramolecular networks which demonstrated both visually healing and recovery of mechanical properties. (3) Polymer blends containing higher degrees of supramolecular cross-link density yielded materials with enhanced mechanical properties. Moreover, after a number of break/heal cycles, these materials were found to retain the characteristics of the pristine polymer blend. A new π-stacking interaction between perylene and the chain-folding diimide motif was also designed, synthesized and characterized before being deployed in healable polymer systems. The polymer blend allowed to be healable and the nature of these materials has been assessed.

A simple route to mechanically robust yet healable polymers via π-stacking has been shown, offering improvements over previous iterations. Furthermore, a new π-stacked motif with perylene has been realized, demonstrating the tailorable nature of the supramolecular motifs described.

**THERMOPLASTICS/THERMOSETS**

**THRM 01 173 Thermal mending in E-glass reinforced Poly(ε-caprolactone)/epoxy blends**
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Thermoplastic/thermoset blends composed of epoxy resin and poly(ε-caprolactone) (PCL) exhibit polymerization-induced phase separation in the presence of anhydride-based hardeners, such as 4,4′-diaminodiphenylsulfone. Above a threshold of 20wt% PCL in the cured blend, a brick and mortar morphology is created which is suitable for thermal mending applications, according to [Luo et al. 2009 (DOI: 10.1021/am800160s)](https://doi.org/10.1021/am800160s): (i) the epoxy bricks are interconnected, limiting the loss in load bearing capacity as compared to pure epoxy, (ii) the PCL mortar expands by approximately 8% in volume upon melting, which enables filling of cracks propagated within the blend. Restoration of mechanical properties should be provided by the re-entanglement of PCL chains in the expanded liquid phase. We investigated the use of such a blend as a self-healing matrix in composites. First, we analyzed the polymerization kinetics of epoxy-PCL blends to obtain the phase diagram of the morphology as a function of PCL content and degree of cure. A PCL content of 22wt% provided the suitable structure, and a modulus lower than that of pure epoxy samples but still above 1.5 GPa at room temperature. Mending capabilities of these blends were assessed in terms of recovery of fracture toughness via Tapered Double Cantilever Beam testing and subsequent heating at 150°C during 30 minutes. Efficiencies above 100% were obtained, indicating a gain in fracture toughness for the repaired samples compared to the virgin ones, due to the PCL path created by the initial crack.

Fiber reinforced PCL/epoxy blends were also produced using an E-glass woven 2x2 twill reinforcement via Vacuum Assisted Resin Infusion Molding. Out of the panels, samples for Mode I Double Cantilever Beam testing were obtained and their mending properties measured. The recovery in fracture properties showed the potential of using these phase-separated blends into composites to repair damage.
The rubber industry is facing a major issue due to the irreversibility of crosslinked networks, which prevents the reshaping or reusing of rubbery objects. Here we report on the heat-triggered healing ability of a chemically crosslinked rubber. Thanks to reversible covalent chemistry, dynamic crosslinks are introduced into an epoxidized natural rubber (ENR) matrix. Our group recently showed that ENR could be efficiently crosslinked by diacrylic acids [1-2]. It was thus easy to introduce functionalities in the rubber by using dicarboxylic acids that contain reversible chemical groups in the middle of the linker. Here disulfide groups were introduced using diithiodibutyric acid as a crosslinker. A dynamic covalent network was thus produced owing to disulfide exchanges.

Self-healing synthetic elastomers were reported, which thanks to the metathesis of aromatic disulfides rearrange at room temperature, meaning that they flow under stress at very long times [3]. Here, the healable properties are triggered by the temperature. Our ENR, chemically crosslinked by aliphatic disulfides, behaves like a classical natural rubber at room temperature, but becomes healable above 150 °C. After grinding to a fine powder, the crosslinked rubber can be reprocessed and recovers most of its initial mechanical properties. The heat-triggered disulfide rearrangement is characterized in terms of stress relaxation, creep/recovery, adhesion tests, and swelling experiments. Comparison is made with ENR samples crosslinked by permanent links.

We design and fabricate a tough elastomer by hybridizing a covalently crosslinked network with reversible hydrogen bonds, circumventing the immiscibility between networks formed by non-polar permanent and polar reversible bonds without solvents. Similar to sacrificial bonds in biological tissues, the reversible bonds break and reform, surprisingly forming crazes that typically exist in plastics and glass; this enables efficient energy dissipation and maintains material integrity upon large deformation, resulting in an elastomer with fracture stress higher than that of natural rubber and the record of tough elastomers formed by interpenetrating covalently crosslinked networks. Our discovery suggests a new route towards tough elastomers, providing a model system to explore the mechanisms of deformation and energy dissipation, and broadens the applications of elastomers.

We report a fast crosslinking system composed of star-shaped polymers [1] suitable for chelation assisted – copper mediated azide-alkyne cycloaddition (ca-CuAAC) [2] – up to now the fastest version of this d-click [3] type reaction. Synthesis of the required internal ligand (p-carboxylic-acid-picolinamide) and introduction to star-shaped polymer is described. Applying in situ NMR-measurements kinetics of low molecular analogues (p-carboxylic-acid-methylester-picolinamide and phenylacetylene (PA)) in a model-click reaction were investigated, including variation of catalysts (CuBr, CuBr(PP3)3, CuOAc, Cu(phen)2(PF6) and the addition of base. Progress of reaction between star-shaped polymers containing an azide moieties and copper-chelating moieties (picolinamide) was monitored via melt-rheology-experiments [4]. Due to the presence of internal ligands and their structural pre-organization of functional reactants an increase of the effective copper-catalyst concentration enables complete crosslinking within 5 minutes at even lower temperatures (< 10 °C). The designed polymers are suitable to act fast, autonomously and highly efficient at lower temperature conditions.

Polymers that repair themselves after mechanical damage can significantly improve their durability and safety. A major goal in the field of self-healing materials is to combine robust mechanical and efficient healing properties. Here, we show that incorporation of sacrificial hydrogen bonds into a self-repairable network dramatically improves the overall mechanical properties. Specifically, we use simple secondary amide side chains to create dynamic energy dissipative polymer networks in a covalently cross-linked polymer network, which can self-heal via olefin cross-metathesis. We envision this straightforward sacrificial bonding strategy can be employed to improve mechanical properties in a variety of self-healing systems.

Thermosetting materials possessing self-healing capability are of particular interest for load-bearing applications due to their potential for enhanced durability and safety. Self-healing systems based on the encapsulated multimalimide solutions within epoxy-amine networks containing pendant furan moieties have been reported [1]. Recently renewable furan-based epoxy systems that contain furanyl building blocks in place of the phenyl rings were investigated [2]. In these systems the furan ring becomes part of the backbone of a polymer network unlike the pendant architecture used for our previous self-healing work. In this investigation, the ability of network backbone furan rings to react with multimalimide molecules in solution was investigated. Reactive solution-based healing was conducted on epoxy networks containing varying concentrations of furan-based di-epoxies. Preliminary results suggest that these systems provide significant capacity for healing.
Self-healing polymers based on reversible crosslinks have been investigated intensively in the last years. Several different approaches have been studied, e.g., reversible supramolecular interactions like hydrogen bonds or metal complexes. Moreover, reversible covalent bonds have been investigated in self-healing materials. The prime example is the Diels-Alder reactions (e.g., furan and maleimide).

We developed an all-in-one system, i.e. one polymer features all required binding units, i.e. the furan as well as the maleimide. Polymer films based on these materials feature a self-healing behavior at elevated temperatures (full recovery of scratches could be obtained after a few minutes). In order to tune the healing temperature different polymeric materials have been investigated. Additionally, the nature of the reversible furan-maleimide-linker was modified. The best systems revealed a similar self-healing behavior at lower temperatures (40 K less).

One possible strategy to obtain lower healing temperatures is the hetero-Diels-Alder reaction. Due to the lack of a large variety of had units (only dithioesters are promising), we investigated Diels-Alder reactions of anthracenes. By the right choice of the anthracene moiety and the other binding unit highly reversible systems can be obtained (in contrast to the classical DA of anthracene and maleimide). In particular, a polymer blend of an anthracene containing polymer and fullerene showed a very good self-healing behavior due to the reversible interactions of anthracene and fullerene. These systems are interesting due to the additional optical and electronic properties introduced by the fullerene.

Recently, intrinsic self-healing covalent polymers based on intramolecular reversible interaction, represented by Diels-Alder (DA) reaction, have been developed. Among the available healing chemistries, disulfide bond is quite attractive because crack healing can be carried out in one-step fashion, rather than two-step one as in the case of DA reaction aided remending. Considering that disulfide metathesis reaction occurs rapidly in the presence of phosphine under alkaline condition, we decided to use phosphine catalyst for developing self-healable and recyclable crosslinked polymer.

On the basis of model experiments we found out that tri-n-butylphosphine (TBP) can effectively catalyze air-insensitive disulfide metathesis in alkaline condition at room temperature. Having been compounded with the phosphine, crosslinked polysulfide exhibits repeated autonomous self-healing capability as characterized by tensile strength restoration owing to dynamic exchange of disulfide bonds. More interestingly, the crosslinked polysulfide can be reshaped and reprocessed at room temperature via TBP mediated reshuffling of the macromolecular networks. Mechanical properties and self-healability of the polymer made from chopped samples surprisingly remain unchanged. In sharp contrast, control specimens free of phosphine catalyst or S-S bonds are neither self-healable nor reproprocessable. The decrosslinking that used to be involved in reclaiming of thermostats is no longer needed during the room temperature reprocessing. Unlike some reversible reaction assisted intrinsic self-healing polymers (polyurethane carrying alkoxyamine, for example), in which re-establishment of intramolecular interaction only takes place among disconnected bonds, reconstruction of crosslinked polysulfide in terms of disulfide metathesis does not necessarily take place at the ruptured points of S-S bonds. The reaction depends on intermediates induced rearrangement of networked chains and proceeds so long as the polymers are in close contact with each other. By making use of this feature, reprocessing of the crosslinked polymer is made possible. The above proposed strategy might open a new avenue for recycling crosslinked polymers.

Chemical reversibility offers versatile possibilities of repeated healing on molecular scale.[1] Thermo-reversible Diels-Alder chemistry has already been combined with the concept of “self-healing”. [2, 3] Although thermo-reversible cross-linking has been known for quite a while[4, 5], intrinsic self-healing polymers that enable crack healing under external stimulation is still not applied on an industrial scale. This work aims at applying such Diels-Alder cross-linking chemistry to industrial rubber compounds. First, a proof of principle for the use of Diels Alder chemistry as cross-linking tool for rubber products is demonstrated. This is done by modifying and cross-linking a commercial ethylene-propylene rubber in two reaction steps. The retro-Diels-Alder reaction causes these cross-links to disconnect at elevated temperatures (150°C) while the Diels-Alder reaction reconnects them upon cooling. This process is fully reversible and can be used to restore fractured parts of polymers.[6] Reversibility of the system was proven with infrared spectroscopy, on the basis of the mechanical properties. Besides healing the fractured sample and retesting to determine healing efficiency, the material was also cut into small pieces and compression molded into new homogeneous samples displaying comparable mechanical properties (impossible for conventionally cross-linked rubbers). The physical properties of the resulting products are comparable to conventionally sulphur and peroxide cured EPDM rubber compounds and are superior compared to their non-cross-linked precursors.

A reversible thermost set exhibiting self-healing properties was studied in this work. By the incorporation of reversible Diels–Alder (DA) covalent bonds using maleimide and furan functionalities a reversible network may be obtained. At elevated temperatures the equilibrium of the DA shifts to the initial building blocks allowing the mobility required to seal the damage. Upon cooling the formation of the adduct is favored cross-linking the network and allowing the recovery of initial properties. The kinetics and equilibrium of the DA/πDA chemistry were studied by microcalorimetry. Based on these results the destruction and rebuilding of the network was studied by rheometry at equilibrium conditions to give an appropriate application window. Mixed reversible/irreversible interpenetrating networks (IPN) were explored, extending the application window and properties of the self-healing networks for coating applications. The dynamics of the reversible bonding is discussed. The mechanical properties of the (ir)reversible networks were further studied by Dynamic Mechanical Thermal Analysis (DMTA) and complemented with Dielectrical Thermal Analysis (DETA). Additionally, a methodology based on thermal analysis was developed to evaluate the repeatability of the healing procedure. This thermal study was complemented by evaluation the self-healing behavior of the material both by mechanical testing and optical microscopy.
ABSTRACTS

Poster Session I
BACTERIA-BASED MATERIALS

BACT P1 121 Rapid quantification of viable spore of concrete self-healing bacteria by a simple spectrophotometric method
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Bacteria used in self-healing of concrete crack need to be embedded into the concrete in the form of dormant spores. However, quantification of viable spores is still a challenging task due to the lack of rapid, efficient and accurate methods. Hitherto, the standard method for enumerating viable endospores is based on colony forming unit (CFU) quantification technique. This conventional method requires serial dilutions, plating, incubation and colony counting, apparently being time-consuming and labor-intensive. Considering that viable spores have a higher refractive index than vegetative cells and the refractivity is subject to decrease during the germination process, we attempted to develop a simple spectrophotometric method for the detection of viable spores. By comparison of the results obtained by both spectrophotometric method and colony counting method, a good linear correlation (R²=0.99) was achieved between viable spore concentration and OD loss under appropriate conditions. To avoid interference from ungerminable spores and vegetative cells, a turbidity complementation strategy of keeping the initial concentration of spore suspensions at the same and relatively lower level was required. The calibration equation developed could be used to predict the viable spore yield produced in a series of fermentation experiments. Our experiment proved that this novel spectrophotometric method was sensitive, rapid, and easy to perform compared to conventional colony counting method.

BACT P2 43 Microbial Self-Healing Concrete: Denitrification as an Enhanced and Environment-Friendly Approach
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Concrete cracks due to its relatively low tensile strength. The cracks are the easiest pathways for liquids and gasses to reach the steel rebar. These fluids mainly contain two major corrosive substances; Cl- and O2 that exacerbate the oxidation of rebar and cause durability problems. Therefore, extrinsic crack repair is inevitable while it is expensive and time consuming. To avoid labour and repair the cracks immediately after their formation, researchers embarked on developing self-healing concrete. Using calcium carbonate precipitation capabilities of microorganisms to repair the cracks is one of the major strategies for developing self-healing concrete. Up to now two different bio-chemical pathways, namely, aerobic oxidation of lactate and ureolysis were used for microbial self-healing concrete. However, they have certain drawbacks such as oxygen limited performance and production of toxic side products, respectively. To achieve an enhanced performance for crack closure in a more environment-friendly way, we studied the denitrification pathway. Two denitrifying strains, Pseudomonas aeruginosa and Diaphorobacter nitroreducens, were encapsulated within expanded clay particles (0.5-2mm) and tested for multiple crack closure (crack range 100-400 µm) in mortar specimens under wet and wet/dry conditions. The crack closure was monitored and confirmed by using light microscope and capillary water absorption, respectively. Under wet conditions specimens with bacteria could completely close the cracks up to 250 µm and partially close the cracks around 400 µm in 2 weeks. After 4 weeks, for 250 µm cracks, mortar prisms containing P. aeruginosa and D. nitroreducens absorbed 40% and 45% less water than reference specimen, respectively, in the first 24 hours of capillary water absorption test. Overall, results indicated that the denitrification pathway works as well as existing methods while it is more environment-friendly. Further studies should be conducted to optimize the amount of healing agent (bacteria) in concrete.

BACT P3 119 Isolation and identification of a calcium-precipitating bacterium and optimization of influential factors
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In the last decade, with the development of concrete science and the requirement of environment-friendly concrete maintenance, bacteria-based self-healing technology for the repair of concrete crack has become one of the research hotspots in the field of civil engineering. Among the influential factors of bacterial self-healing process, calcium precipitating activity of bacteria is of high importance. In this work, screening of bacteria with high calcium precipitating efficiency was carried out and the effect of variable factors on bacterial-induced calcium precipitation in concrete simulating solutions was further investigated. Thirteen morphologically different strains were obtained from mangrove sediment and soda lake sediment. The calcium precipitating activities (CPA) of the strains were evaluated, and strain H4 exhibited the highest CPA value. Strain H4 was identified as bacillus species based on the 16S rDNA sequence analysis. Further, the effect of variable factors on calcium precipitation of strain H4 was evaluated. The result showed that sodium lactate and sodium nitrate were the best carbon source and nitrogen source for the precipitation of calcium ion, respectively. When the concentration of sodium lactate was above 10 g/L, the calcium precipitation reached the top and remained stable. The increase of initial concentration of sodium nitrate from 0 to 1.5 g/L led to a significant increase of calcium precipitation, whereas the concentration of sodium nitrate more than 2 g/L inhibited the calcium precipitating process. Under the optimal conditions obtained above, strain H4 achieved its maximal calcium precipitating activity at initial pH 10.6 with the suitable spore concentration being 4.0×107 spores/ml. The study will lay a foundation for the further application of bacterial self-healing technology in the repair of concrete crack.

BACT P4 126 A waterproof epoxy resin microcapsule for the encapsulation of self-healing bacterium
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Nowadays, the development of self-healing technique in concrete based on microbial calcium carbonate precipitation has been becoming very promising. However, it is necessary to set up a waterproof protection strategy for embedded self-healing bacteria in the concrete during casting, hydration period and service life before crack occurred. Epoxy resin has been widely used in concrete as the crack repairing agent, but so far no microcapsule was made from epoxy resin to encapsulate bacteria for concrete self-healing purpose. In this study, epoxy resin (ER), a waterproof material, was used to fabricate microcapsule by interfacial curing reaction to encapsulate an alkaliphilic spore-forming bacterium. Trimethoxy silane was employed as silane coupling agent KH792. The technical feasibility of encapsulated spores, the influence of three kinds of curing agent (silane coupling agent KH792, DMP-30 and m-Xylylenediamine), which were used as curing agent for the fabrication of microcapsule, on the calcium precipitation activity (CPA) of the bacterium were studied. Further, microcapsule morphology and CPA was observed by Scanning Electron Microscopy (SEM). Afterwards, the thermal stability and thermodisflow temperature were determined by TGA thermal analyzer. Moreover, the CPA of broken/unbroken microcapsules was evaluated. In addition, water resistance was evaluated by adding microcapsules in the water for 4 h, 15 d and 30 d. The results showed that compared with unbroken microcapsules, higher CPA was achieved by breaking the microcapsule to release the bacterium, suggesting good protection for the encapsulated spores. Three curing agents showed nearly similar influence on the spores, while KH792 performed relatively better, and thus was used to fabricate microcapsule with the core/shell weight ratio being 1:1. Our results also indicated that ER microcapsules could keep unbroken in the water for more than one month. Therefore, we put forward this waterbreak epoxy resin microcapsules could be potential for the application of self-healing concrete.
Self-healing concrete based on bacteria and nutrients immobilized by ceramite
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Small cracks in concrete may develop into large cracks to decreased service life of concrete structures. It is therefore necessary and advisable to restrict the development of early age small cracks promptly. This study provided a bio-restoration method to improve the self-healing effect of the cement-based materials cracks. Ceramite carrier was used to immobilize bacteria, while substrate and nutrients mixed evenly were immobilized into original carrier. Then the ceramite was mixed with cement, sand and water to prepare self-healing materials. The surface of the specimens before and after curing was investigated by staining them. Also apparent water permeation coefficient was applied to characterize the repairing effectiveness of different types of Group specimens. Experimental results showed that plenty of calcium carbonate generated on the section surface after 21 day of curing; the apparent water permeation coefficient of the specimenschanged slightly. Compared with other microbiological methods that used to repair the cracks, the flexural strength can be increased about 60% to 85% by testing the mechanical properties. The results indicated that this kind of bio-restoration method was effective in improving the repair speed and depth of cracks of cement-based materials.

BACT P6 125 Trigger of self-healing process induced by EC encapsulated mineralization bacterium and healing efficiency in cement paste specimen
Bing Liu (liubing0708@szu.edu.cn), Jinlong Zhang, Jinlong Ke, Xu Deng, Biqin Dong, Ningxu Han, Feng Xing, Shenzhen University CN

The purpose of this work is to evaluate self-healing behavior of encapsulated mineralization bacterium in cement paste specimens. Bacterial spores were encapsulated by using ethyl cellulose (EC), and then microcapsules were introduced into cement paste specimens during mixture period. After 14 day hydration period, the specimens were subjected to a splitting test to make crack. Breakage of microcapsules upon cracking and successful mineralization was visually observed with X-ray Computed Tomography (XCT) in three dimensions. Micro-morphology of healing material produced during the process was investigated by Environmental Scanning Electron Microscopy (ESEM) and X-ray energy dispersive spectroscopy (EDS). Furthermore, efficiency of self-healing performance was evaluated with some parameters such as healed crack width, water permeability and chloride ion penetration resistance. The XCT results showed that formation of crack successfully triggered the breakage of embedded microcapsules. Subsequent production of calcium carbonate confirmed by EDS indicated activation of encapsulated mineralization bacterium. Compared with the specimens without embedded bacterium, the healed crack width of specimens embedded with bacterial microcapsules was higher, and the water permeability and the penetration depth were much lower, suggesting effective self-healing of concrete crack can be achieved by introducing encapsulated mineralization microorganisms into concrete structures.

BACT P7 143 The study on carbon dioxide captured and mineralized by cement-based materials loaded with bacteria
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There are quantities of technologies to solve the problem of globe greenhouse effect, while the most significant method is capturing and storing carbon dioxide. Carbonic anhydrase, a kind of metalloenzyme, exist in the body of animals, plants and certain microorganism widely, which is known as one of the fastest rates biocatalyst. It can catalyze carbon dioxide to bicarbonate observably. Inspired by carbonic anhydrase, cement-based materials are types of mediums to fix and consume carbon dioxide efficiently. Taking advantage of extensive existence of buildings, load microorganism which secret carbonic anhydrase on the surface of cement-based materials. In this way, it could capture and mineralize carbon dioxide from the air into calcium carbonate. As the consequence, it can strengthen surface compactness of cement-based materials, resist external erosion and improve durability of buildings.

CEMENTITIOUS MATERIALS

CEMT P1 178 New insights into autogenous self-healing in cementitious materials
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It has been reported that water is one of the most essential factors for autogenous self-healing. On the one hand water in cracks serves as a reactant and on the other hand as a medium in which reaction products can precipitate. If cement paste is not saturated with water, in the healing process water in the crack can migrate into the bulk paste. By now the effect of migration of water from cracks into the bulk paste on self-healing is still not clear yet. Nuclear Magnetic Resonance (NMR) tests were performed to investigate water migration from cracks into the bulk paste in this work. The changes of water content and water distribution in the bulk paste were quantified by NMR. NMR results confirm that once water penetrates into the crack from the outside environment, it migrates into the bulk paste. However, after 22-hour exposure of the crack to water, the fronts of water profile hardly move. The water content of cement paste adjacent to the crack surfaces decreases instead. By knowing the change of the amount of water, further hydration of unhydrated cement was determined and the volume of reaction products of further hydration caused by extra water was calculated. It was found that in a cement paste with w/c ratio of 0.3, a layer of very dense paste is formed adjacent to the crack surfaces after 220-hour exposure of the crack to water. Such a dense layer paste can prevent from the ingress of aggressive ions into the concrete matrix and decrease the risk of degradation of concrete. The observation of the dense layer cement paste adjacent to the crack surfaces provides a new insight into autogenous self-healing.

CEMT P2 83 Development and characterization of novel self-healing material for cementitious materials
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Due to its high compressive strength and relatively low cost, concrete is still one of the main materials used in the construction industry. However, cracking tends to occur in concrete as a consequence of its relatively low tensile strength. Since these cracks can provide entry channels for potentially aggressive liquids and gasses which can result in concrete deterioration, a mechanism for self-healing is very beneficial to improve the durability of concrete. In the present work, a new polymer-based healing agent has been developed to be applied in self-healing of cementitious materials. Several key prerequisites of the healing agent, such as viscosity, curing time, swelling capacity and elasticity were evaluated. The healing agent was manually injected into cracks of mortar samples to evaluate its potential to seal concrete cracks. After curing of the healing agent, the crack width was then increased by 50, 100 and 150% in order to evaluate its elasticity and strain capacity. Interestingly, a strain of at least 150% could be achieved as no differences were observed in the microscopy images of the healed crack after each stepwise elongation. Therefore, the developed healing agent is a promising candidate to seal dynamic cracks in structures under cyclic load. Furthermore, the results indicate that the developed polymer has favorable self-healing properties including an adequate curing time, viscosity and mechanical properties.
The search for self-healing materials is justified by the increasing sustainability and security needs of structures. The presence of small cracks in structural concrete, which could accelerate the degradation process and diminish its service life, is unavoidable due to its heterogeneous nature. A method to enhance self-healing in concrete is the use of crystalline admixtures (CA), which are hydrophilic products formed by chemical active substances, cement and sand. This research analyzes the self-healing properties of young concrete specimens for autogenous and CA-based healing under different exposure conditions. Two types of concrete were studied: a control mix, and a mix containing the CA (with a dosage of 4% by weight of cement). Six exposure conditions were studied: water immersion at 15°C, water immersion at 30°C, water contact with a water head of 2 centimeters, wet/dry cycles, humidity chamber, and laboratory conditions. Self-healing capability was evaluated by measuring the permeability of concrete specimens before and after the healing period. Cylindrical specimens were pre-cracked by means of splitting test at the age of 2 days, and their permeability measured at the age of 3 days and after 42 days in the healing exposure. The range of studied crack widths was limited to 300 micrometers. From the tests, the self-healing reaction was confirmed for both mixtures for exposures in direct contact with water. Exposing just one surface to water increased healing rates, but only the crack in direct contact could be sealed. Finally, slight differences were measured between both mixtures, with a higher stability for concrete with CA. To sum up, only cracks in direct contact with water could heal, achieving higher healing rates when the specimens were immersed in water. Ambient humidity was not enough to produce healing either for control concrete or concrete with CA.

**CEMT P3 84 Study of the self-healing behavior of early-age cracks in concrete with crystalline admixtures under six environmental exposures**

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Concrete is the most widely used construction material over the word because of its high compressive strength and low cost. However, it is sensitive to crack formation because of its limited tensile strength. These cracks endanger the durability of concrete buildings as aggressive liquids and gases may penetrate into the matrix along these cracks and cause further damage. Hence, inspection, maintenance and repair of concrete cracks are indispensable. For these reasons, self-healing ability would be desirable for concrete. In this research, cementitious hollow tubes were produced by extrusion and used as healing agent containers that were embedded in the mortar matrix to obtain self-healing properties. Based on the results of preliminary mechanical tests, sodium silicate, potassium silicate and Primal (a commercial acrylic resin) were first selected as healing agents. To determine their efficiency, three-point bending test was performed on samples with the different healing agents and load, as well as, stiffness recovery indexes were determined. It was first observed that modulus of rupture and elastic modulus were not affected because of the presence of the capsules inside the samples with respect to plain mortar samples. The best results were achieved with the sodium silicate solution. The Load Recovery Index, ranged from +7.4% to +27.6% and the Stiffness Recovery Index, ranged from +5.8% to +37.5%, one month after damaging the samples. After six months of rest, the Load Recovery Index ranged from +17.1% to +70.9% and the Stiffness Recovery Index, ranged from +15.7% to +53.6%. A longer time for repairing seemed to increase the efficiency of sodium silicate as a healing agent.

**CEMT P4 258 Self-healing Capability of Ultra-High-Performance Fiber-Reinforced Concrete (UHP-FRC)**

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UHP-FRC (ultra high performance fiber reinforced concrete) is being successfully developed in the last decade, which shows the high strength and high durability due to its very dense microstructures. Moreover, in corporation of fibers in the mix design of UHP-FRC exhibits the high ductility and high energy absorption capacity. The high ductility of UHP-FRC materials shows pseudo-strain hardening behavior and multiple cracking after the occurrence of the first crack under uniaxial tension stress. Generally, presence cracks is not desirable from durability viewpoint. That is, presence cracks should be recovered in order to sustain durability of UHP-FRC. Here, self-healing phenomena might be strongly helpful to coexistence of two different characteristics (i.e. the formation of calcium carbonate crystals on the crack surface and re-hydration of un-hydrated cement particles). In this study, the potential of self-healing capability of UHP-FRC was investigated. As a result, it is confirmed that permeability of cracked UHP-FRC could be recovered by precipitation of calcium carbonate crystals and re-hydration of remained un-hydrated cement particles in the matrix. Additionally, combination of steel fibers and synthetic fibers could be positive way to improve self-healing capability.
A new generation of multifunctional cementitious materials with spatial damage sensing capacity is being developed in the context of protection and health monitoring of structures. This work aims to establish the relation between cracking or healing within cementitious materials with their electrical properties. Electrical impedance spectroscopy was conducted on multifunctional cementitious composites before damage, at different levels of damage, and during self-healing. The results revealed that the complex impedance is strongly influenced by crack width and crack number, both of which will change during the self-healing process. In addition, a new equivalent electrical circuit model was proposed for simulating changes in the electrical properties of the material system during damage and healing. This study shows the promise of the cementitious material for direct sensing of its own damage state and healing level.

Tokyo Metro Co., Ltd. operates and maintains a subway system of about 195 km consisting of nine lines. Tunnels account for about 85% of the total length, and most of them are located under the center of Tokyo. Water leaks have begun to be found in some of them where they cross under or run near rivers, channels, canals or reclaimed lands. Although water stop measures have been taken on the affected areas using considerable amounts of budget every year, many of the repaired areas exhibit the same problem again. It is urgently needed to develop new materials and techniques to stop water for proper long-term maintenance of these structures. The authors conducted test construction in an existing subway tunnel to stop water leaking from cracks, using self-healing materials. The self-healing materials, which are under development at the University of Tokyo, consist of ordinary Portland cement as the main ingredient and three types of admixtures: CSA-based expansive agent, geo-material; and chemical admixture of the carbonate group. Three different techniques were used in the test construction, depending on the amount of leak water. For locations with a small amount of leakage, holes with diameters of about 15 mm were drilled into a depth of about 30 mm at intervals of 30 to 50 mm along the crack and filled with self-healing cement paste, and the surface was finished self-healing cement mortar. Locations with a large leakage (about 14 liters per minute) were treated by a combined technique using inorganic waterstop agents for cracks, which was placed before the placement of self-healing cement paste. The results showed a high potential applicability of the materials and techniques tested in the study for use in subway tunnels.

Corrosion is one of the most important reasons for the degradation of reinforced concrete structures, especially for those exposed to de-icing salt or marine environment. Cracking is an inevitable characteristic for concrete, which could be induced by shrinkage, external load or some other reasons. Cracks provide preferential pathways for aggressive agents (oxygen, carbon dioxide, chlorides, and water) to reach the surface of steel bars and accelerate corrosion initiation. However some research found that, for cracks smaller than a particular width, self-healing (caused by further hydration, carbonation and precipitation of small particles, etc.) may effectively close the crack and thereby slow down the corrosion rate or inhibit the corrosion process. In this paper, the effect of self-healing of cracks on corrosion is studied. Ring shaped mortar samples reinforced with 6mm steel bar were cracked with different crack widths, and then subjected to high humidity environment for one month, three months and six months to get different degree of self-healing. The self-healing degree of cracks was assessed by air flow measurements through these cracks. Then the samples were exposed to cycles with 2 days of wetting in salt solution and 12 days of drying under 20°C and 50% relative humidity. After several months, the samples were broke and steel rings inside were extracted out to compare the corrosion degree. The experiment is still in progress and the results will be presented in the full paper.

Crack in concrete is one of the biggest problems in terms of functionality, durability and aesthetics of infrastructures. Therefore, maintenance and repair of cracked concrete are also very important for civil engineering fields. So, various repair materials and techniques have been already suggested and many types of repair materials are currently being used. In this study, innovative repair methods based on crack self-healing technologies using cementitious materials were suggested. Especially, this study focused on two primary issues: (1) experimental and analytical design of new cementitious repair materials with self-healing capabilities, (2) development of crack repair materials, matching repair materials and their new repair methods. Therefore, various repair materials were examined for new repair materials with self-healing capability applied to crack sealing method and to patching repair method.

The project detailed in this paper aims at a thorough characterization of the effects of crystalline admixtures, currently employed as porosity reducing admixtures, on the self healing capacity of the cementitious composites, i.e. their capacity to completely or partially re-seal cracks and, in case, also exhibit recovery of mechanical properties. The problem will be investigated with reference to both a Normal Strength Concrete (NSC) and a High Performance Fibre Reinforced Cementitious Composite (HPF RCC). In the latter case the influence of flow-induced fibre alignment will also be considered in the experimental investigation. With reference to either 3-point (for NSC) or 4-point (for HPF RCC) bending tests performed up to controlled crack opening and up to failure, respectively before and after exposure/conditioning of stiffness and stress bearing capacity will be evaluated to assess the self healing capacity. In a durability-based design framework, self-healing indices to quantify the recovery of mechanical properties will also be defined.
Nowadays, concrete is the most widely used construction material in the world. Despite many technical and economic advantages, it has some drawbacks such as brittle behaviour under thermal or mechanical loading. This results in crack initiation and propagation in concrete elements that consequently, requires periodic maintenances. It is estimated that using self-healing concrete can save approximately € 80 million of the maintenance costs for concrete bridges, tunnels and retaining walls in the European Union. However, the bottleneck for valorisation of self-healing concrete is developing suitable capsules which (1) can survive during concrete mixing; (2) are compatible with the healing agent and resist the high pH environment of concrete; (3) break upon crack formation while show enough bonding with surrounding concrete and (4) do not negatively affect the properties of fresh and hardened concrete. Up to now, most research has been done by using glass tubes for proof-of-concept which is not appropriate for practical applications. This paper evaluates the feasibility of using different types of polymeric tubes including polyactic acid (PLA) and polymethyl methacrylate (PMMA) with and without impact modifiers as carriers of healing agent for self-healing concrete. Different properties of these polymeric materials, including impact performance and mechanical behaviour, were evaluated by using dynamic mechanical thermal analysis, impact and tensile testing. Furthermore, tensile strength of polymeric tubes, their bonding to concrete, compatibility between healing agents and tubes, survival rate of capsules during concrete mixing and breakage of embedded polymeric capsules upon crack formation in concrete were studied in detail.

**CEMT P12 248 Comparative Study on Different Polymer Tubes as Carriers of Healing Agent for Self-Healing Concrete**
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The experiment focuses on the study that micro-crack of concrete structure is easily repaired by self-healing technology. Although Self-healing technology is widely studied in construction filed recently, it is rarely applied to repair and maintenance method. Since there are many problems in repair and maintenance work at construction site, it is necessary to develop the material to work simply and easily. Therefore, the surface treatment repair method has developed because micro-crack (less than 0.3mm) of concrete is easily repairing and applied to self-healing technology. The usability of crack repair stick, one of the surface treatment repair methods, is to verify equally between repaired surface and existing surface on crack at construction site. On the other hand, in order to evaluate the self-healing property by using crack repair stick, which contains self-healing agents is experimented, such as relative dynamic modulus of elasticity, water permeability test, observation of microscope and SEM analysis, when generating re-crack at repaired surface. As a result, it has verified that durability enhanced by experiment and SEM analysis. Therefore, it has verified that crack repair stick, which contains self-healing agents is capable of autonomic healing on re-crack of concrete structure.

**CEMT P13 93 Ideal material properties for capsules or vascular use in cementitious self-healing materials**
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K. Van Tittelboom, Ghent University, BE

Self-healing in cementitious materials, i.e. concrete, has a huge potential towards reducing maintenance and repair costs and increasing the service life time of concrete structures. The biggest advantage of self-healing concrete is that small cracks, which provide access to hazardous gasses and liquids, are healed and slow structural degradation is prevented. Several techniques are trending in the field of self-healing concrete, self-healing using bacteria, self-healing using a vascular system and self-healing using capsules. Focusing on the latter, an encapsulation material is needed. This paper describes the ideal properties of such an encapsulation material.

**CEMT P14 262 Self-healing of dynamic cracks in reinforced concrete based on encapsulated polymer precursors**
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While the existing research on self-healing concrete focuses mainly on the strength regain achieved with self-healing of cracks, this study aims at assessing the sealing of cracks and the strain capacity of elastic polymers fit for healing of dynamic cracks (e.g. due to traffic loads or cyclic temperature variations). Different types of liquid polymer precursors were used as healing agents after encapsulation in cylindrical glass capsules. The precursors used cover a wide range of properties in terms of viscosity and foaming potential, leading to distinct mechanical properties after curing. A series of test procedures were developed to assess the performance of the healing agents at a laboratory scale in small mortar specimens containing encapsulated precursors. Realistic cracks of approximately 300 μm were used throughout the study. The performance of the different systems varied significantly, with viscosity being an important parameter for the dispersion of the precursors and proper sealing of cracks. Moreover, it was shown that a large foaming effect is detrimental. Distinct failure mechanisms were observed after widening of healed cracks, resulting from the differences in elasticity, structure and adhesion of the polymers bridging the crack walls. A discussion on the encapsulation techniques is also included, highlighting the challenges and shortcomings of those that show potential for up-scaling the concept and allow the use of encapsulated polymer precursors in conventional concrete production methods. The research has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 309451 (HEALCON).

**CEMT P15 171 Feasibility study on the surface treatment repair method using crack self-healing technology for micro-cracking of concrete**
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SeungWonYang, SERIC R&D Center, SERIC Co., Ltd, Seoul KR

The experiment focuses on the study that micro-crack of concrete structure is easily repaired by self-healing technology. Although Self-healing technology is widely studied in construction filed recently, it is rarely applied to repair and maintenance method. Since there are many problems in repair and maintenance work at construction site, it is necessary to develop the material to work simply and easily. Therefore, the surface treatment repair method has developed because micro-crack (less than 0.3mm) of concrete is easily repairing and applied to self-healing technology. The usability of crack repair stick, one of the surface treatment repair methods, is to verify equally between repaired surface and existing surface on crack at construction site. On the other hand, in order to evaluate the self-healing property by using crack repair stick, which contains self-healing agents is experimented, such as relative dynamic modulus of elasticity, water permeability test, observation of microscope and SEM analysis, when generating re-crack at repaired surface. As a result, it has verified that durability enhanced by experiment and SEM analysis. Therefore, it has verified that crack repair stick, which contains self-healing agents is capable of autonomic healing on re-crack of concrete structure.
CEMT P16 135 Porosity Change and Crack Self-Healing of Cementitious Material with Gamma-Dicalcium Silicate by Carbonation Reaction
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Dicalciumsilicate (C2S) occurs in several polymorphic forms: α, α’, α”, β and γ. Most of them are stable in the pure state only at elevated temperatures and it is merely the γ form that is thermodynamically stable at room temperature. Each polymorph shows different reactivity with water. Statements on the reactivity of the γ polymorph of C2S in the presence of water vary between “non-hydraulic” and “essentially non-hydraulic” to “slowly hydraulic”. As a result, most of the studies focus on the prevention of β to γ transformation and the ions that can stabilize β rather than the improvement of γ-C2S hydraulic properties. Despite the slow hydration kinetics of γ-C2S in water, the reactivity of this phase could be enhanced through the action of strong alkalis that stimulate its dissolution and result in the formation of binding phases. This method, known as alkali activation, has been receiving substantial attention for a wide range of materials, blast furnace slags included. By another study as a carbonation curing method, Belite-rich cement (low heat Portland cement) was reported that pores can be reduced, leaching resistance improved, and strength increased by accelerated carbonation. For crack healing of cementitious materials with calcium carbonate compounds by carbonation of γ-C2S. This paper describes the effects of gamma-dicalcium silicate [γ-C2S] that reacts with carbon dioxide during carbonation curing and porosity change, adds to the strength although no hydration reaction occurs and densified pore structure. We studied on the properties of carbonated cement paste with gamma-C2S. After carbonation, compressive strength of blended sample made with 10 wt. % replacement ratio of gamma-C2S would be also improved. This finding would be due to the reason that the gamma-C2S reacts with CO2 and then produces CaCO3 phase, leading to the densification of cement matrix. Porosity of cementitious materials with γ-C2S in accelerated carbonation curing was reduced about 33% less than porosity of OPC in air curing. Phases of cementitious materials with γ-C2S in accelerate carbonation curing are Calcite and Vaterite, compare with phases OPC in air curing are Portlandite, Alite, Belite Quartz and others.

CEMT P17 28 Flow Characteristics of Autogenic Healing agents in Cementitious Materials
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Recent advances in the field of self-healing technology have significantly improved the potential performance and durability of cementitious materials. Autonomic healing agents, such as cyanoacrylates, resins and expanding foams are being used widely in self-healing cementitious materials. However the use of autogenic pozzolanic-based materials such as Ground Granulated Blast Furnace Slag (GGBS), Pulverised Fuel Ash (PFA), Metakaolin and Silica Fume in the healing process has received far less attention. These healing agents, in fluid suspension form, may be encapsulated and embedded in the cementitious matrix and will, upon rupture, flow through the cracks by capillary action. The advantage of these autogenic healing agents is their long term compatibility with the cement matrix. This study investigates the flow characteristics of two autogenic healing agents (PFA and Metakaolin) in discrete macro cracks, which are representative of early-age cracks in structures formed from cementitious materials. A benchmark study is reported which examines the characteristics of flow in planar voids between two glass plates and provides data on suspensions of autogenic healing materials. Moreover, the time dependent surface tension, contact angle, viscosity and Hagen Poiseulle (H-P) flow characteristics are also studied to identify the nature of the interaction between the healing agents and the cementitious material. Knowledge of these characteristics is vital for ensuring the successful and timely capillary transport of healing agents to damage sites.

CEMT P18 134 Precipitation of Calcium Compounds by Fructan from Microbes and Properties for Crack Self-Healing of Cementitious Materials
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A typical durability-related phenomenon in cementitious materials is crack formation. While larger cracks hamper structural integrity, also smaller sub-millimeter sized cracks may result in durability problems as particularly connected cracks increase matrix permeability. As regular manual maintenance and repair of concrete constructions as cementitious materials is costly and in some cases not at all possible, inclusion of an autonomous self-healing repair mechanism would be highly beneficial as it could both reduce maintenance and increase material durability. Therefore, many studies, the functionality of various self-healing additives are investigated in order to develop a new generation of self-healing concretes. In the present study, we were investigated on the formation of solid calcium compounds by a specific bio-chemical additive named Fructan. Fructan from microbes is a single polymer that is connected over millions of fructose. Fructan is possible to produce solid calcium compounds by reaction with calcium ions. The mechanism of crack healing in cementitious materials with Fructan presumably occurs through metabolic conversion of Fructan to calcium carbonate and/or solid calcium compounds what results in crack-sealing. This biochemically mediated process resulted in efficient sealing of sub-millimeter sized (0.15 mm width) cracks. So, we are investigated on the formation conditions of solid calcium compounds by reaction of Fructan and calcium ions for crack self-healing of cementitious materials. 

CEMT P19 144 The Study on a new cementing system of consolidating soil by using carbon dioxide
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As we know, China is the major consumer of coal and producer of cement. We are going to be under pressure of reducing the emission of carbon dioxide in the "Copenhagen" era. Furthermore, unfavorable geological condition influences the engineering feasibility and safe reliability of building seriously, while high energy consumption and high emission of carbon dioxide exist in the production of traditional cement kind of soil solidifying agent. According to the above question, this paper generated ideas from the bio-mineralization phenomenon in nature, and tried to make a new mineralization gel system of MgO - CO2 - H2O form which sped up the reaction through biotechnology to solidify soil more quickly. Meantime, this paper realized the transformation storage of carbon dioxide by solidifying soil with carbonate minerals.
Blast Furnace Slag (BFS) is a waste product of industrial steel production and a very common additive in the cement industry in Northern European countries. However, cementitious materials made from BFS cement, particularly CEM III/B, are very susceptible to carbonation. Recent investigations have shown that the surface application of Na2PO3 solution as pre- and post surface treatment can improve the microstructure and surface durability of carbonated cementitious materials with a high BFS concentration. Significant improvements have been observed in mechanical characteristics of concrete surface and frost salt scaling resistance. Our latest study focuses on the influence of cementitious pore solutions activated with Na-MFP and their impact to liquid and solid phase formation during carbonation and self-healing blast furnace slag cement products. Here we investigate the occurring solid phases by x-ray powder diffraction and quantitative phase analyses and put our results in context with the observations obtained from pore solution reactions with solid cement phases. On the basis of previous studies we are aiming to develop an autogenous self-healing mechanism for BFS cementitious products containing coated and powder-pressed pellets made from Na2PO3F from a mineralogical point of view in order to obtain a sustainable and strong building material with a long lifetime.

**CEMT P21 290 Self-healing expansive oil well cement**

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Cement has been used for decades as the default zonal isolation material in oil and gas wells. However, Portland cement systems have characteristics that often adversely affect their sealing capacity such as unfavorable rheological properties for proper cement placement, shrinkage during setting, and poor bonding to steel. In particular, the micro-cracks at the cement-casing interface caused by sustained casing pressure and high temperature environment usually result in high costs for maintenance and repair as well as potential safety risks. This research focuses on the experimental development of enhanced oil and gas well cement formulations that combine the use of expansive additives and self-healing components to deliver the required rheological and other properties under downhole conditions focusing on elevated temperatures. Mineral expansive additives will be utilized as well as microencapsulations self-healing agents that are able to function under the elevated temperatures and release the self-healing cargo under the appropriate trigger mechanisms such as cracking or chemical ingress. The work will involve testing of a range of properties including the rheological properties, mechanical properties, expansive performance, self-healing mechanism and recovery of mechanical strength as well as impermeability and other durability performance will be investigated. The microstructure will be analyzed and linked to the properties above. This research is particularly useful for oil well cements where it is impossible to assess the effectiveness of the cement placement operation and the sealing process as well as deterioration over time. Hence a cement system that would respond to a range of damage including cracking and ingress of hydrocarbons or CO2 would have a huge impact on enhancing the safety and reliability of cementing in oil and gas wells particularly in the long term and in abandonment operations.

**CEMT P22 301 Novel Alginate-Waste Glass Composites for Self-Healing Mortars**

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The development of cement-based materials capable of autonomic repair of cracks is relevant to the design of more durable structures. Due to the large scale use of concretes and mortars, the incorporated self-healing agent needs to be cost-effective and environmentally benign. In this respect, a candidate self-healing composite of alginate (a natural, renewable polymer) and waste glass has been evaluated for its potential to repair cracks in young mortars. The composite was prepared by mixing 50 µm waste glass fragments with a 5 wt% aqueous alginate solution (glass:alginate = 1:8). The mixture was extruded through a 2 mm bore and gelled in a 5 wt% calcium chloride solution for 30 mins. The resulting composite tubules were dried to constant mass in air at 40 ºC. Ordinary Portland cement mortars (cement:sand:water = 1:3:0.45) and those containing 4 wt% alginate-waste glass composite (AWG) were mixed and cast into 25 x 25 x 150 mm stainless steel molds. Specimens were demoulded after 24 h and cured at 95% relative humidity at 20 ºC. Two-week old control and AWG mortars were pre-cracked by 3-point bending to 90% of their maximum load. The impact of AWG on the 28-day flexural strength and toughness of the mortars was then evaluated via 3-point bending to failure. The strength recovery of the AWG mortar specimens was found to be 36% greater than that of the control (Fig. 1). A concomitant increase in toughness of 92% was also observed for the AWG mortar. The recovery of strength and toughness are attributed to the pozzolanic reaction of the exposed waste glass fragments when cracks propagate through the AWG composite.

**MICROCAPSULES: CEMENTITIOUS**

**MCAP-CEMT P1 109 Preparation of Cu2+–P(VIm–MMA) complex shelled microcapsule with and its respondent behavior to carbonate ion in water**

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Most of the microcapsules used in self-healing materials are stress-triggered, but in many instances, the response of microcapsule to ionic concentration is expected, and a lot of industrial applications bank on the corresponding microcapsules. For example, pH-sensitive microcapsules could be used as drug carriers with controlled release in medical treatment; chloridion-triggered microcapsules in concrete enable the marine construction from chloride attack. In this paper, a microcapsule sensitive to carbonate ion was prepared and researched. It is shelled with a complex made up of copper ion and a copolymer with dangling imidazolyl ligand. When the microcapsules encounter carbonate ion in water, the copper ion is carried off to form copper carbonate precipitate, meanwhile the complex is decomposed to release the content. The copolymer is synthesized from 1- vinyl imidazole and methyl methacrylate, by a simple radical polymerization, and the microcapsule is prepared by a solvent evaporation progress. It’s believed the result microcapsule could be applied in concrete to protect the cement matrix against carbonization.
Ion-sensitive microcapsule has attracted much attention of the researchers in biologic and medicinal field, but most of them are triggered by pH value. In this paper, chloridion-responsive microcapsule was designed and synthesized for the chemical self-healing materials, such as the seawater-corrosion resistant concrete.

The microcapsule is sheled by polymethylmethacrylate (PMMA), in which small particles of lead sulfate (PbSO₄) are embedded as chloridion switches. It should be stable in freshwater but not in seawater. When chloridion appears in water, the PbSO₄ precipitant will dissolve because of the following complexing reaction: PbSO₄ + 4Cl⁻ → PbCl₄(2-) + SO₄(2-) Distinctly, the response time rests with Cl-concentration. Trigger experiment shows it’s about 5 hours in 3.5% NaCl artificial sea water. The microcapsule was prepared by a simple solvent-evaporation method. The process is consist of three steps: (1) mixing core materials, PMMA polymer and fine PbSO₄ powder in dichloromethane (DCM) to obtain a suspension; (2) emulsifying the suspension in water; (3) removing DCM from the emulsion by evaporation at 39°C. The result microcapsule presents very good sphere shape, narrow particle size distribution and uniform PbSO₄ embedment.

A chloridion-respondent capsule walled by silver alginate complex (Ag-alg) was prepared by piercing method, and the trigger processes in NaCl aqueous solution with different concentrations of 1wt%, 2wt%, 3wt%, 4wt% were examined respectively. After embedded in cementitious matrix, the responsive behavior of capsules was observed and analyzed X-ray computed topography (XCT).

Encapsulation technology is a promising low-cost means to achieve self-healing function for some materials. Embedding capsule in matrix could repair the hidden inner micro-cracks that are difficult to be detected and inaccessible for repair. It is believed capsule will play an important role in autonomous healing field. Steel reinforced concrete, for instance, is prone to induced corrosion by chloride ions, a simple way to solve the problem is just mixing corrosion inhibitor into concrete, but most of them will be lost in the cement slurry making process because of dissolution or diffusion. One feasible method is to encapsulate the inhibitors and then embed the capsules in materials. When a micro-crack appears, the microcapsule will break under stress to release the inhibitors. Unfortunately, the wall of capsules is not always apt to fracture. It depends on the interface bonding strength between the wall of capsule and the matrix. Furthermore, in the occasion without significant cracks emerging, chloride ions may spread through innumerable nano-channels, which exist extensively in cementitious matrix. In that case, the steel may be corroded but capsules do not start to work yet. So it is necessary to develop a kind of capsule responsive to chloride ions directly. In this article, a chloridion-sensitive complex, silver alginate (Ag-alg), was select as the wall material to form the capsule. The response of this capsule to chloride ion is proved to be very reliable and quick. As the capsules are fabricated by injecting sodium alginate into silver ion solution though a tiny hole, the size is very uniform. The diameter of capsule is about 2.5mm. The trigger process was observed with Environment Scanning Electron Microscopy (ESEM) and Confocal Laser Scanning Microscope (CLSM). Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS) characterized the products after the trigger reaction.
MCAP-CENT P7 45 Investigation of a novel self-immunity system in cementitious materials with calcium oxide microcapsules
Guohao Fang (fgbfsz@ccloud.com), Biqin Dong, Ningxu Han, Feng Xing, Shenzhen University, CN

The paper presents work toward to study a brand new self-immunity system in cementitious materials with calcium oxide microcapsules. This self-immunity system is based on the ratio of [Cl-/OH-], which is an important criterion to indicate probability of rebar corrosion within cementitious materials. Based on this theory, a novel kind of microcapsule with calcium oxide was synthesized successfully. In order to analyze the self-immunity effect of reinforcing steel bar within the cementitious materials in a qualitative and quantitative way, a new effective non-destructive testing method was put forward in the paper. This new testing method is based on the electrochemistry test and X-ray computed tomography test. Based on the different marine environment, the standard reinforced motor with microcapsules were put in different solution with different chloride ion, and using the new method to tracking analyze the self-immunity effect for different specimens in different simulation environment.

MCAP-CENT P8 97 Chloridion response of the microcapsule shelled with polystyrene-cuprous chloride composite
Guangming Zhu (gzhu@szu.edu.cn), Yongxing He, Jiaoning Tang, Ningxu Han, Feng Xing, Shenzhen University, CN

Microcapsules with response to chemicals have a variety of potential applications, for example, embeddng chloridion- triggered microcapsule containing repairing agent or corrosion inhibitor in steel reinforced concrete is considered to be an effective measures to protect marine construction against chloride attack. In this paper, a chloridion- sensitive microcapsule was designed and synthesized based on the following reaction: CuCl2+2OH-→[Cu(OH)]2. This microcapsule was consists of polystyrene-cuprous chloride (PS- CuCl2) composite shell and epoxy resin core. It forms in a solvent-evaporation process at 40°C. Soaked the result microcapsule in 3.5% NaCl artificial sea water, cuprous chloride was dissolved in a short time.

MCAP-CENT P9 141 Determination of the rupture stress of a microcapsule and the Young’s modulus of its shell materials by nano-indenter
Guangming Zhu (gzhu@szu.edu.cn), Fusong Xiao, Jiaoning Tang, Ningxu Han, Feng Xing, Shenzhen University, CN

As a core/shell structure, the deformation of microcapsule under stress is consisting of two parts: the shell deformation and the structure deformation. It will complicate the calculation of Young’s modulus of shell materials and rupture stress of whole microcapsule if the data is acquired by a nano-indenter. In this paper, a method was developed to determine the ruptured stress form load-displacement curves, and a novel working mode of the nano-indenter was employed to measure the Young’s modulus of the shell materials by using a Berkovich nano-indenter continuously contacting the sample surface.

MCAP-CENT P10 142 Investigation into mechanical- performance of a signal DCPD/PF microcapsule with nano-indenter
Guangming Zhu (gzhu@szu.edu.cn), Fusong Xiao, Jiaoning Tang, Ningxu Han, Feng Xing, Shenzhen University, CN

An individual phenol-formaldehyde (PF) microcapsule containing diclofenac potassium (DCF) as healing agent was selected as a sample to investigate the relationship between deformation and mechanical properties of the micro-ball with core/shell structure. Based on the load-displacement curves obtained with nanoindenter, a computational method was set up to deduce the Young modulus and hardness of shell, and cracking load of the core/shell microcapsule. Indentation size, residual wall thickness and the ball diameter difference before/after loading were measured by an optical microscope with super depth of focus to determine the amount of plastic deformation. It’s found there is a linear dependence between plastic deformation amount and the wall thickness of shell. The cracking load does not change with particle size d and wall thickness δ severally, but varies inversely with the ratio of d/δ. The Young modulus of PF wall rests with the wall material itself only, has nothing to do with d or δ.

MCAP-CENT P11 59 The effect of polymeric microcapsules on the mechanical properties of cementitious materials
Petros Giannaras (pg419@cam.ac.uk), Abir Al-Tabbaa, University of Cambridge, UK

Concrete is able to self-heal limited-width microcracks mainly through the continued hydration of cement paste as well as the precipitation of calcium carbonate under favourable conditions. This autogenic self-healing capability can be enhanced through the addition of microcapsules for autonomic self-healing. Here, encapsulated healing agents are released when microcapsules propagate within the cementitious matrix and lead to rupture of the microcapsule shell. A range of both chemical and bacterial cargo materials have been investigated in the literature. The first step in ascribing whether an autonomic self-healing system incorporating microcapsules is feasible is to quantify the initial change in intrinsic properties of the cementitious material due to the dispersion of microcapsules. Of course, an initial enhancement in mechanical properties is preferred. However, a reduction may be acceptable if it can be outweighed by an increase in material longevity as a result of the autonomic self-healing enhancement. The calibration of experimental literature shows no clear trend in the effect that the addition of microcapsules has on the initial mechanical properties of cementitious materials. Some authors have reported an increase, whilst others have reported a decrease, in compressive strength, flexural strength and elastic modulus at varying microcapsule proportions. This incoherence is partly due to the variation in experimental procedures as well as the difference in raw material and microcapsule properties. The effect of different types of polymeric microcapsules on the mechanical properties of both cement paste and mortar was investigated through experiments and modeling. Scanning electron microscope images were used to characterise microcapsules and to obtain their size distribution. Survivability, along with rupture due to propagating microcracks within the cement matrix, was also confirmed in cracked specimens. The techniques used in this work facilitate the assessment of microcapsules used for autonomic self-healing up to the healing agent release stage.

MCAP-CENT P12 140 Chloridion-triggered microcapsule for self-healing concrete application
Guangming Zhu (gzhu@szu.edu.cn), Yujie Guan, Jiaoning Tang, Ningxu Han, Feng Xing, Shenzhen University, CN

Sodium monofluorophosphate (Na2PO3F) microcapsule shelled with sodium polyacrylate (PAS) double coordination with Ag+ or/and double chelate with Cu2+ was prepared by spray-drying process, and its respondent behavior to chloride ion in 3.5wt% NaCl artificial sea water was examined with stereomicroscope. It’s found microcapsule shelled with PAS-Ag is very susceptible to hydrosoluble chloride ion, while microcapsule shelled with PAS-Cu has no response, but it possesses hard and brittle shell. The shell consists of the mixture of PAS coordination or chelate with Ag+ or Cu2+ is compromised in the performance of Cl- response and mechanics. The shell strength increases with the incremental Cu2+/Ag+ ratio in central ions, while the sensitivity to chloride ion on the contrary. When Cu2+/Ag+ is over 2:1, the microcapsule has no answer to chloride ion. This microcapsule shelled with PAS-(Ag+ + Cu2+) complex could be used in self-healing concrete to spontaneously protect rebar against chloride attack.
ABSTRACTS

Poster Session II
BIOMATERIALS

BIOM 1 116 Mussel inspired surface functionalization of electrospun nanofibers for wound dressing application
Melisa Samarikhalaj (amin.ghavaminejad@gmail.com), Amin Ghavaminejad, Chan Hee Park, Cheol Sang Kim, Chonbuk National University, KR

Recently, the practical applications of mussel inspired catechol-containing polymers have been greatly expanded due to their fascinating chemical properties. In this study, we present a facile one-step electrospinning process to synthesize electrospun mussel-inspired copolymer, poly (dopamine methacrylamide-co- methyl methacrylate) (MADO) with enhanced antibacterial activities after surface functionalization with silver nanoparticles (AgNPs). The assembly of silver nanostructures was driven by the catecholic moiety. The morphologies and structures of the nanofibers were analyzed by field emission scanning electron microscopy, Fourier transform infrared spectroscopy, and X-ray diffraction. The nanofibers had a smooth surface with an average diameter of 800 nm. The diameters of the AgNPs were in the range of 15-22 nm. We also evaluated the biocompatibility of the nanofibers, particularly their cytotoxicity to human skin fibroblasts and potential to cause primary skin irritation. The in vitro antibacterial activity and in vivo wound healing capacity of the nanofibers were also investigated. The nanofibers significantly inhibited growth of Escherichia coli bacteria. The nanocomposite nanofibers accelerated the rate of wound healing over that of the control. The results of our in vitro and in vivo animal experiments suggest that catecholic nanofibers show potential to be used as a bioactive wound dressing.
BIOM P2 226 Swelling kinetics of mucins after granular release
MD ARIFUZZAMAN (arFuzzaman20sp@gmail.com), Abdullah, Lubna, Kesimer Mehmet, University of North Carolina at Chapel Hill, NC USA

Gel forming mucins are polyanionic biopolymers with very high molecular weight. They are spontaneously released by cells in order to form uniform viscoelastic gel material called mucus which is essential for maintaining the innate defense mechanism of the epithelial systems including human airways. Gel forming mucins are synthesized in endoplasmic reticulum and subsequently multimerized and post-translationally modified in the golgi apparatus, and then packaged into secretory granules under low pH and high calcium concentration. Swelling/hydration of the mucins in the granule and after granular release is one of the essential steps for understanding the mechanism of forming transportable mucus gel which is essential for airway clearance. Based on this motivation, in this work we have focused on the study of swelling kinetics of mucins in secretory granule of Calu-3 cells which represents a differentiated airway cell line culture. Calu-3 cells are cultured on glass bottom dishes, and treated with a buffer containing 10 mM Ionomonc to stimulate to granular secretion. Mucin granules were labeled with 10 mM Acridine Orange before 100 mL of the buffer was added to the apical side of each culture. After adding the stimulating reagent the cells start releasing mucin granules and as soon as the granule is exoxytosed, it swells very rapid and membrane ruptures. Finally, the content of the granule, compact mucin is partially then fully swollen, in other words stretched. In this research work, swelling kinetics of mucin granule is monitored by obtaining time lapse images in a confocal laser scanning microscope. We surmised that post-exoctic mucin swelling behavior in normal epithelial cells would be different from the diseased cells like cystic fibrosis (CF), chronic obstructive pulmonary disease (COPD) and/or Asthma etc. It is expected, in diseases, the compact mucins would follow different swelling rate compared to normal. Secretd mucins in diseases, therefore, would not be completely linearized which might greatly affect the formation of evenly mucus coat on the epithelial cell surface. So far, progress in this area is largely challenged by lack of suitable mucin stains during synthesis as well as suitable real time imaging methods. The technical challenges arise from the fact that secretion and post-exoctic swelling process is very rapid, often fully completed in fractions of a second.

BIOM P3 302 Neurite Behavior of Primary Hippocampal Neurons on Micropillar Arrays
Matthew Park (mata425@gmail.com), Daewha Hong, Insung S. Choi, KAIST, Daejeon, KR.

Topographically modified cell substrates especially, are potent stimuli for neurite outgrowth since neurons, like most adhesive cells, respond strongly to the physical features of their environment. Studies on neurite guidance traditionally use line-based structures such as grooved quartz, aligned nanofibers, or even cell-mimetic patterns. However, most guidance studies have solely used continuous, line-based topography as cell substrates; the effective utilization of interrupted topographies such as pillars is rare, despite their unique effects on neuron, including enhanced axonal development and high neurite affinity. In this work, we devised pillar arrays that would direct neurite outgrowth based on the topographical preferences of neurites. The micropillar arrays were able to induce neurite alignment in primary hippocampal neurons. This system of micropillar arrays can contribute to the development of neural prostheses, artificial neural networks, and clinical neuroregenerative techniques.

COATINGS & PAINTS

COAT P1 237 Encapsulation of Maleimide-Based Healing Agent and Reversible Diels-Alder Chemistry for Self-Healing and Corrosion Prevention
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Protective epoxy coatings for metal substrates are used for wear resistance and physical protection against environment conditions that may result in physical or chemical changes, such as corrosion. Previous work done by Pratama et. al investigated the use of encapsulated solutions containing maleimide-based healing agents for self-healing of furan functionalized epoxy networks through reversible Diels-Alder chemistry. Results from these studies show that the use of phenyl acetate as a solvent, and the concentration and structure of maleimide healing agent has an effect on the physical and chemical bonding across the crack surface. We used a urea-formaldehyde (UF) encapsulation technique to create capsules with a diameter of ≤ 300 um, containing phenyl acetate-maleimide solutions. This healing system allowed for multiple healing cycles and increased load recovery. The phenyl acetate-maleimide healing agent and Diels-Alder reactions can similarly be used in the design of self-healing polymer systems for coatings. Specific protective epoxy coatings require a thickness of 30-40 um, thus capsules with an approximate diameter of ≤20um are desired. This can be achieved by increasing shear rate and by incorporating ultrasonication processing to the UF encapsulation procedure. The purpose of this work is to study the effect of capsule size on healing efficiency in thin films that are representative of coatings.

COAT P2 137 Crack Self-Healing Property by Revival of Silicate Modified Cross-Linked PVA Film for Waterproofing of Concrete
Myongshi Song (msong0422@kangwon.ac.kr), Hyunjin Song, Woongjin Kim, Sol-a Bak Kangwon National University, Samcheok-City, KR

PVA is a synthetic hydrophilic polymer widely used in various areas, including foods, lacquers, resins and cosmetics industries. Silicate compounds as Tetraethoxysilane (TEOS), m ethyloethoxysilane (MTE) and polyvinyl alcohol were used to synthesize hydrophobic and multi-function PVA/SiO2 organic-inorganic hybrid material based on sol-gel method. The cross-linked Si-O-Si units and PVA chains in hybrid form organic-inorganic hybrid networks and produce reinforcing and toughening effects. Moreover, the outstretched methyl groups on the surface and the multi- pores in the body contribute hydrophobicity and air permeability. This hydrophobic and multi-pore PVA/SiO2 organic-inorganic hybrid material can be used to prepare functional composite materials such as environmental friendly packaging film and mulching film and others. We studied on the synthesis of modified PVA with silicate compounds and its application for crack self-healing of waterproofing film in concrete construction. Revival process of waterproofing film for waterproofing of concrete construction can show figure 1. If waterproofing film is destructed, destructed waterproofing film is swelling by meeting water and modified PVA film, and then, destructed film will be revive by swelling of modified PVA film. For this, aqueous polyvinyl alcohol (PVA) solution was modified by using hydrophobic triethoxysilane (TEOS). The material and mechanical properties, contact angle, water vapor transmission rate (MVTR) and oxygen gas transmission rate (O2TR) of the film samples fabricated by modified PVA-silicate (MPS) solutions were investigated. The glass transition temperature (Tg) of the MPS films was slightly increased. The film prepared with MPS, of which the swelling and solubility were measured to be 178% and 0%, respectively, showed improved water-resistance. Figure 2 is contact angle and water permeability property. We confirmed efficiency of waterproofing by revived modified PVA film in waterproofing system.
Self-healing materials have the ability to repair or prevent further damage autonomously, where and when it occurs. A successful strategy for designing self-healing materials relies on microencapsulation of liquid healing agents which are dispersed throughout a bulk polymer or coating. Here we explore the use of electrospun core-shell fibers to sequester healing chemistry for protective coatings. In coaxial electrosprinnning, two immiscible liquids are pumped through the inner (self-protective core) and outer (polymer shell wall) coaxial needles. A high voltage is applied on the needle tips to electrostatically draw out core-shell fibers (submicron size in diameter). We have developed a polyisiloxane based coating for steel containing two types of core-shell fibers. Fiber type A contains a stoichiometric mixture of low molecular weight silanol terminated poly(dimethylsiloxane) (PDMS) with a poly(diethoxysiloxane) crosslinker and fiber type B contains a crosslinking initiator, with the poly shell of poly(vinyl alcohol) for both fiber types. The electrospun fiber layers are then sprayed with a silicone conformal coating to bind the fibers to the steel substrate to produce a conformal coating. When the coating is mechanically damaged, the two fiber types release their liquid core materials to fill the damaged region, crosslink, and restore the protective coating layer. Characterization of fibers and coating include SEM, TEM, confocal fluorescence microscopy, and FTIR. Development of new coatings synthesized by core-shell electrosprinnning will provide corrosion protection to metals, thus increasing material lifetime and performance.

FIBER-REINFORCED COMPOSITES

FIBR P1 169 Strengthening of fiber-reinforced self-healing ceramics
Kazuki Baba (baba-kazuki-nw@ynu.jp), Wataru Nakao, Daisuke Maruoka, Yokohama National University, JP

One of the candidate materials for turbine blade is proposed as continuous fiber reinforced self-healing ceramic composites (shFRC). The shFRCs consist of three components, which are oxide fiber bundle, oxide matrix and self-healing agent interlayer. As the self-healing is generated at only the interlayer, it is necessary that crack propagation is led into the interlayer. As a result, shFRCs exhibit complex fracture behavior. To enhance mechanical strength of shFRCs for actual applications, defect size in fiber bundles and thickness of interlayer, which has the lowest strength in shFRC, are needed to be decreased. In the present study, some attempts were made to attain the above objections. As a result, it was succeeded that the new type of shFRC having 7 times higher strength than that of proto-type shFRC was developed.

FIBR P2 68 Modified Nanoﬁllers for Self-Healing Materials: Nanoclays and Polyhedral Oligomeric Silsequioxanes
Wilton Osim (wilton.osim@chemie.uni-halle.de), Wolfgang H. Binder, Martin Luther University, Halle-Wittenberg, DE

Composite materials made from surface modified nanoﬁllers can be used for the realization of structural aeronautic components, providing very good self-healing properties and flame-retardancy. Herein, we describe the attempt towards the development of surface-modified nanoﬁllers (nanoclays (Na MMT) and polyhedral oligomeric silsequioxanes (POSS)), displaying catalytic effects, in turn acting as self-healing agents for the activation of self-healing functions at low temperature. The immobilization of different types of catalysts (Ru, Cu) onto the surface of nanoﬁllers was conﬁrmed via XPS, EDX and FE-SEM analysis. The activity of these functionalized nanoﬁllers has been tested both in model ROMP and click reactions. The use of surface modiﬁed ﬁllers with catalytically active sites in the development of self-healing materials is projected to effect an improvement in the mechanical and physical properties of the overall material including enhanced modulus and thermal stability as well as enhanced impact resistance and flame retardancy.

FUNCTIONAL APPLICATIONS

FUNC P1 94 Polymer - Particle Dual Network: Towards concomitant self-healing & load-bearing properties in intrinsically SH materials
Zhen Liu (hydrozhen.liu@gmail.com), N.A.M. Besseling, S.J. Picken, Delft University of Technology, Delft, NL

Intrinsically self-healing (ISH) nanocomposite was produced by mixing the supramolecular elastomer polyborosiloxane (PBS) with organically modified nanoclay (OMNC). The PBS and OMNC govern the self-healingness and mechanical rigidity separately, based on a principle which we denote "separation of timescales". Above the percolation threshold (~1% by weight), OMNC particles provide the nanocomposite with not only improved impact strength, but also a second relaxation process at much longer time scale. A combination of WAXD and rheology investigations suggests that particles establish a rigid skeleton in the dynamically cross-linked PBS medium, without significantly confining the PBS molecules. In such composites, creep due to a sustained load is prevented and the rapid self-healing process remains unaltered. In contrast, natural clay self-assembles with PBS via hydrophilic interaction, and therefore it results in weaker nanocomposites, as well as longer self-healing time.
CHAR P2 114 ON THE CORRELATION OF MOLECULAR DYNAMICS TO HEALING KINETICS OF NATURAL RUBBER
Marianella Hernández (m.hernandezsantana-1@tudelft.nl), S.J. García, S. van der Zwaag, Delft University of Technology, Delft, NL

Although much effort has been devoted to the creation of self-healing elastomers based on supramolecular chemistry, limited attention has been paid to the self-healing of conventionally vulcanized rubbers. Healing is especially challenging in vulcanized rubbers, where the confinements imposed by cross-links restrict polymer chains to form new bonds across former (pre-)fractured surfaces.

This research addresses the development of vulcanized Natural Rubber (NR) compounds with self-healing properties, based on reversible sulfide bonds incorporated into the rubber network. While it is relatively easy to demonstrate the occurrence of self-healing (i.e., the restoration of mechanical properties) the underlying physico-chemical reactions at molecular level are less easy to be monitored. In the present work, BDS was used to follow the molecular dynamics evolution with the healing process.

Sulfur cured NR compounds were prepared according to different vulcanization systems (conventional and efficient). The compounds were vulcanized at different temperatures and times so the potential influence of the sulfide bonds and distribution in the healing properties of NR could be evaluated. Special attention was paid to the overall molecular dynamics of these materials by means of BDS measurements (see Figure 1). A systematic research on the relaxation behaviour of these elastomers elucidated the role of the sulfide bonds in the key healing reactions. This new insight into the character of both the network structure and the sulfide bonding by means of dielectric processes was found to be very useful for monitoring the healing process at a scale close to the relevant molecular processes, understanding the role of the various chemical processes involved. The method and analysis developed may be of relevance to the study of self-healing properties of elastomeric self-healing systems yet to be developed.
MECHANOCHEMISTRY

MECH P1 292 Mechnochemical activation of the Amid Bond
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Martin K. Beyer, Leopold-Franzens-Universität Innsbruck, Innsbruck, Austria

The mechanical stability and the degradation of individual chemical bonds can be investigated by single molecule force spectroscopy and quantum chemical calculations. Here we have investigated the stability of an amid bond in aqueous solution at high forces: On a carbon surface we have functionalized a primary amine. An amid bond was formed by coupling the primary amine with single molecules of carboxymethylated amyllose (CMA). The force dependent lifetimes of this molecule were investigated with single molecule force spectroscopy method on the atomic force microscope (AFM) in force clamp mode. Individual CMA molecules were stretched with different clamp forces and at different temperatures until a bond scission was observed. Activation energies and Arrhenius pre factors were obtained by using the Arrhenius equation. Force dependence of the reaction rate constant was evaluated with different models. The resulting reaction rate constants show nearly zero force dependence at room temperature. It was found that between 0.8 nN and 1.6 nN the Arrhenius pre factor and activation energy exhibit only a small force dependence. The reaction pathway was investigated by performing force dependent density functional theory (DFT) calculations using the External Force is Explicitly Included method. In accordance with the literature, it was found that the base catalyzed hydrolysis of the amid bond is the most likely reaction. The resulting kinetic parameters, Arrhenius pre factor and activation energy agree with the experiments. The calculations show that the base catalyzed reaction is preferred if an external force is applied. Additionally, it was found that because of the applied force the bond breaking mechanism is changed. In completely we see a mechnochemical heterolytic bond scission supported by a base catalyzed peptide bond.

MECH P2 293 Illuminating the Mechanical Memory of Filled Elastomers with Dioxetane Mechnoluminescence
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Stephen L. Craig, Duke University, NC USA

Dioxetane mechnoluminescence is a powerful new way of visualizing stress distributions in polymeric materials. First demonstrated in 2012 (1), force applied to polymer chains can induce the scission of bis(adamantyl)-1,2-dioxetane mechnophore units incorporated within the polymer backbone. Both singlet and triplet excited adamantanes are formed from the cleavage, which relax to the ground state by the emission of light or transferring their excitation energy to an acceptor. Dioxetane mechnoluminescence has since been used to investigate the deformation and failure of a wide variety of polymeric materials (2),(3). In this work, the dioxetane mechnophore was used to probe the “mechanical memory” in filled elastomers, also known as the Mullins effect. It has been well known for decades that the addition of small amounts of filler particles to elastomers can improve their mechanical properties significantly, but that this also begets other changes to their mechanical behaviour, namely stress-softening and hysteresis. The origins of these effects are still hotly debated. Cyclic uniaxial tensile tests on dioxetane-functionalized silica-filled poly(dimethylfloxane) (PDMS), an important class of filled elastomers, suggest that covalent bond scission only becomes an important contributor to the observed mechanical hysteresis at higher strains (>140%); below this threshold, mechanical behaviour appears to be determined by non-covalent mechanisms, such as the deadsorption and readsoption of polymer chains on the filler particles. Straining pre-conditioned samples at different orientations relative to the original tensile direction also revealed a strong anisotropy in the strain-induced covalent scission.

MICROCAPSULES: POLYMERS

MCAP-POLY P1 265 Microcapsules for self-healing and their advanced characterization
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Amandine C. Crabbe, Herman Terryn Free University of Brussels, BE
Filip Du Prez, Ghent University, Ghent University, BE

Microcapsules are core-shell structures where an active compound that can be a solid, liquid or gas is surrounded by a protective membrane. Microcapsules are already used for a variety of purposes in industries such as food, pharmacy and agriculture. A more recent development of the microcapsules is to use them in self-healing materials. Deterioration and weakening of polymeric materials lead to the formation of cracks and during the formation of a crack microcapsules in the matrix should break and release their reactive liquid content, allowing the material to recover its strength. The synthetic routes for the formation of core-shell structures involve mainly the emulsification of the active agent into an immiscible phase upon mechanical stirring and the shell formation by in situ or interfacial polymerization onto the droplet surface. Melamine-formaldehyde (MF) and polyurea (PU) microcapsules are widely used for self-healing purposes as they provide the desired mechanical and physical properties. These capsules need to survive the processing conditions, but they should break when the material is damaged. In this study we provide detailed characterization of the microcapsules regarding their shell strength, thickness and flexibility, their behaviour in the epoxy matrix and the encapsulation efficiency of the core as well as core-shell interaction by using SEM, Focused Ion Beam (FIB) and Raman spectroscopy.
MICROVASCULAR SYSTEMS

MVAS P1 154 Fabrication of Self Healing Epoxy based Composites by Tri-axial Electrospinning Technique
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Multi-walled healing fibers with a novel architecture are fabricated through utilizing a direct, one-step tri-axial electrospinning process to encapsulate dicyclopentadiene (DCPD) as healing agent of fibers with two separate protective walls. The schematic representation of tri-axial electrospinning system and Scanning Electron Microscope image of tri-axial hollow fiber are given in Figure 1. Polymers with different polarities are selected as middle and outer wall of fibers in which polyacrylamide (PAAm) as an intermediate layer provides inert media for DCPD monomer encapsulated inside of fibers while polymethyl methacrylate (PMMA) with dispersed catalyst particles as an outer layer is compatible with epoxy matrix. Low affinity of middle wall polymer and self-healing agent minimizes the interaction of healing agent with surrounding media that results in extended efficiency and life-time of healing functionality. Moreover, multi-layered structure of fibers provides selective dispersion of catalysts into the outer layer of tri-axial fibers instead of direct catalyst impregnation into epoxy matrix. Integration of catalyst particles at outer layer of fibers reduces the required amount of extremely toxic and expensive catalyst, prevents the deactivation of catalyst during the manufacturing process, and more importantly, guarantees the presence of catalyst in the crack area in which healing agent is released from fibers. The most exceptional property of healing systems based on electrospun fiber with continuous and uniform morphology is the repetitive release of healing agent in damaged area and the multiple healing of same damaged areas. PMMA as an outer layer is also compatible with epoxy matrix and provides great improvement in mechanical performance of epoxy based composite. Encapsulation by tri-axial electrospinning is based on physical forces to form the core/sheath structure and additional wall in fiber structure increases the lifetime of healing agent and open up new opportunity in development of chemistry and design of self-healing materials.

MVAS P2 240 Microvascular self-healing within automated composites manufacturing
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Konstantin Eftatisidis, Aurora Flight Sciences, University of Massachusetts Lowell, Lowell, MA USA

Microvascular self-healing composite materials offer scope for improved lifetime and system-level performance in aerospace and other advanced composites applications. To date, microvascular self-healing capability has been primarily restricted to manual fabrication techniques. By contrast, Automated Fiber Placement (AFP) increasingly forms the backbone of aerospace composites manufacturing, but the lack of a viable self-healing material systems suitable for AFP hinders their manufacture and adoption by industry. In this work, we present efforts to integrate self-healing microvascular structures into unidirectional carbon prepreg materials suitable for AFP processing and to characterize the resulting structures’ self-healing and thermal management performance. Specifically, sacrificial filaments and carbon nanotubes (CNTs) are integrated within AFP-compatible prepregs with the aim of healing large damage volumes and maintenance of interlaminar properties, respectively. Sacrificial thermoplastic filaments, which degrade in a post-cure cycle to embed hollow synthetic microvascular networks within a composite structure, are extruded in continuous lengths suitable for direct spoiling onto unidirectional carbon fiber prepregs or as an input for fused deposition modeling (FDM) for subsequent additive manufacturing onto the prepreg surfaces. AFP-related parameters, such as feed rate and roller pressures are correlated with filament quality and the embedded microvascular features. The colocation of vertically-aligned carbon nanotubes and the microvasculature within the interlaminar regions is investigated for integration of self-healing functionality without degradation of the interlaminar strength properties. Self-healing performance is evaluated within a double cantilever beam geometry and the synergistic effect of resistive heating on the healing efficiency is quantified.

SUPRAMOLECULAR POLYMERS

SUPR P1 206 Heal-on-Demand by Local Heating in Ionomeric Nanocomposites
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The research interest on remote-controlled multiple responsive materials has increased over the last few decades. Magnetic nanoparticles have the potential to convert magnetic energy of external alternating fields into thermal energy. The combination of magnetic nanoparticles with soft materials offers new possibilities towards smart adaptive materials that can be manipulated by external magnetic fields. In particular, the local heat dissipation by magnetic nanostructures in oscillating electromagnetic fields (OEMF) provides the option to increase the temperature locally and thus stimulate dynamic processes, e.g. for self-healing. In this work, we systematically investigate the influence of the size, shape, composition and magnetocrystalline anisotropy of the magnetic nano-antennas in an acrylate-based ionomeric elastomer on the heating and healing characteristics. Furthermore the influence of the particle on the dynamic and mechanical properties of the used ionomers is taken into account. The locally dissipated thermal energy in the particles’ environment triggers a thermal transition in dynamic polymeric matrices activating the self-healing process. In comparison to known thermally activated systems, the incorporation of nanoscopic heat sources leads to a faster response and allows the contactless, remote-controlled triggering of the sample shape. Under optimized conditions, a particle volume fraction as low as 0.05 vol% is sufficient to reach a healing efficiency of 90 % and higher after 15 min of irradiation.

THERMOPLASTICS/THERMOSETS

THRM P1 159 Tough elastomers by hybridizing covalent and reversible networks
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We design and fabricate a tough elastomer by hybridizing a covalently crosslinked network with reversible hydrogen bonds, circumventing the immiscibility between networks formed by non-polar permanent and polar reversible bonds without solvents. Similar to sacrificial bonds in biological tissues, the reversible bonds break and reform, surprisingly forming crazes that typically exist in plastics and glass; this enables efficient energy dissipation and maintains material integrity upon large deformation, resulting in an elastomer with fracture stress higher than that of natural rubber and the record of tough elastomers formed by interpreting covalently crosslinked networks. Our discovery suggests a new route towards tough elastomers, provides a model system to explore the mechanisms of deformation and energy dissipation, and broadens the applications of elastomers.
THRM P2 52 Acylyhydrazones as reversible covalent crosslinkers for self-healing polymers
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In the last few years, self-healing materials have gained more and more attention. Self-healing materials are able to heal inflicted damage and to recover the mechanical properties. Therefore, the lifetime and reliability of these materials can be increased. In literature several intrinsic self-healing materials, in particular polymers, are reported where the self-healing behavior can be achieved by the incorporation of specific structural elements. For this purpose, reversible covalent bonds (e.g., based on the Diels-Alder reaction or disulfide bonds) or weaker non-cova lent interactions (e.g., hydrogen bonding, ionic interactions or metal-ligand interactions) are utilized. The acylyhydrazone functionality was chosen to promote self-healing in covalently crosslinked polymer films, because the reversibility of this functionality has been well investigated in solution. An acylyhydrazone linker, which was functionalized with two polymerizable groups, was designed and copolymerized with different commercially available methacrylates in bulk. The resulting polymer films were characterized by different methods and the self-healing behavior was studied in detail (Figure 1). Thereby, it could be demonstrated that an acylyhydrazone content of 10 mol% is required to achieve self-healing properties. The expected mechanism of the self-healing process was confirmed by temperature dependent FT-IR spectroscopy as well as solid state NMR.

THRM P3 232 Reactivity and properties of Cross-linked Polymers Containing Diarylbibenzofuranone in Hard or Soft Domain
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Dynamic materials that respond to surrounding environments have been widely studied, because they show fascinating functions and properties such as structure reorganization and healing by external stimulation. In the field of polymer science, one of the approaches to dynamic materials is the insertion of dynamic covalent linkages into the skeleton of polymeric materials. Although there have been many examples of dynamic covalent linkages, we focused on a new class of dynamic covalent linkage, diarylbibenzofuranone (DABBF). DABBF derivatives are in equilibrium of dissociation and combination at room temperature (Figure 1). Arylbibenzofuranone (ABF) radicals formed from DABBF show blue color and tolerate oxygen. Recently, we have demonstrated self-healing, autonomous network reorganization, and mechanochromism of polymers with DABBF. However not all polymers containing DABBF units show self-healing function and mechanochromism. There are many questions about the relationship between reactivity of DABBF units and macromolecular structure. Herein, we report reactivity and properties of two types of cross-linked polymers containing DABBF in hard domains (one hard type sample) and in soft domains (three soft type samples) prepared by a sol-gel method. Hard type sample and soft type samples were prepared from DABBF-alkoxysilane derivatives and poly(butyl acrylate) having dialkoxyisilyl groups at the both ends (Si-PBA). Soft type samples (1, 2, and 3) were prepared from poly(butyl acrylate) having DABBF in the center of polymer chains and trialkoxyisilyl groups at the both ends, and the molecular weights between cross-linking points in 1, 2, and 3 were different. Hard type samples behaved like a conventional chemically cross-linked polymer. On the other hand, soft type samples showed unique properties such as healability of thermoplasticity, and mechanochromism attributed DABBF units. These results indicated that the location of DABBF units in the cross-linked polymers significantly dominates their reactivity and properties.

THRM P4 128 Electrically induced healing of a Diels-Alder-CNT polyurethane composite
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Thermoreversible [4+2] Diels-Alder chemical bonds are widely used in the field of intrinsic self-healing polymers 1,2. These reversible covalent bonds can be incorporated into polymeric matrices to reform broken bonds upon heating. The most commonly used Diels-Alder moieties are the furan (dieno) and the maleimide (dienophile) because of their low temperatures of activation (Tretro-DA = 120°C, TDA = 50°C, cf. Figure).

In this communication, we introduce a new Diels-Alder based self-healing polyurethane composite containing multi-walled carbon nanotubes (MWNT). The self-healing polyurethane was synthesized through reactive extrusion process (REX). With this technique, a polyurethane based pre-polymer bearing maleimide pendant groups, obtained by polycondensation in bulk between hexamethylene disocyanate, dodecanediol and a diol bearing a maleimide function, is crosslinked with a difuran coupling agent in order to form thermoreversible networks. This manufacturing process of self-healing polymers by REX offers several advantages to other methods such as the short residence time (synthesis time), the lack of use of solvents, the good dispersion of the MWNT into the polymeric matrix and its scalability into a real industrial process. The MWNT were introduced to promote the healing of the polymeric matrix based on the electrical properties of the MWNT: by application of a current, the temperature of the polymer rises by Joule effect and leads to the necessary mobility and DA reaction necessary to close cracks. As monitored by IR-camera, the electrically-induced temperature increase is in the range of the retro-Diels-Alder reactions. Moreover a temperature increase at the edge of the crack was observed leading to a very localized crack closure by zipping effect. The healing efficiency of this new polyurethane nanocomposite was attested via scratch test and IR camera, while a rheometer coupled with the FT-IR spectroscopy was used to study the reversibility and the kinetics of the Diels-Alder reactions occurring under heating/cooling cycles.
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