

# REMEMDABLE POLYMERIC MATERIALS USING REVERSIBLE COVALENT BONDS

Giuseppe R. Palmese\* and Amy M. Peterson  
Drexel University, Department of Chemical & Biological Engineering  
Philadelphia, PA 19104

Robert E. Jensen  
U.S. Army Research Laboratory  
Aberdeen Proving Ground, MD 21005

## ABSTRACT

Materials that can recover mechanical properties following failure offer increased safety and service life. Moreover, successful development of such systems would reduce factors of safety required in design thus reducing weight. Inspiration for remendable materials comes from nature where the ability to heal is a characteristic of living organisms and a prime example of autonomy. The development of self-healing polymeric material systems could therefore enable new multifunctional composite systems used in military applications. Two approaches for healing polymer networks have captured much attention. In one method, polymer networks are made to self-heal by adding particles filled with uncured resin. The resin held within the particles is released upon crack formation and cures to mend the damage. The other mechanism for healing relies on inherent reversibility of bonds found designed into polymer networks. The work to be presented is part of the Drexel-ARL Army Materials Center of Excellence (MCOE) program for polymers.

Our approach to design self-healing composites combines advantages of healing via encapsulation and healing via reversible bonds. Incorporation of a healing agent allows for crack healing while maintaining the desirable physical and mechanical properties of the base thermoset. Reversible bonding of the healing agent provides the ability to crack heal cracks multiple times.

We report on the development of two healing systems for epoxy-amine thermosets based on the thermoreversible Diels-Alder reaction of furan and maleimide. In one, crack healing of a traditional epoxy-amine thermoset is induced by thermally reversible crosslinking of a secondary phase. The secondary phase can be in the form of microspheres or fibrous mats. In the other, furan functionalization of an epoxy-amine thermoset allows for *in-situ* crack healing of this thermoset with a bismaleimide solution. Both phenomena occur at room temperature and minimal pressure and significant load recovery is possible multiple times in a given location.

In both methods significant strength recovery is observed. In the second close to complete recovery is observed. In this case strength recovery is postulated to be the result of both physical and chemical bonding across the crack surface. Physical bonding is caused by solvent-mediated swelling and subsequent interlocking of crack surfaces, while chemical bonding results from the Diels-Alder reaction of furan and maleimide. This form of the Diels-Alder reaction is reversible, forming a ring structure at room temperature and reforming the respective diene and dienophile between 60 and 90°C.

The degree of strength recovery is linked to a detailed kinetic analysis of the reversible reaction obtained using near IR spectroscopy. Moreover, the polymer network design is based on this analysis and takes into account intrinsic kinetics as well as diffusion limitations that limit the approach to equilibrium compositions at processing and healing temperatures.

## 1. INTRODUCTION

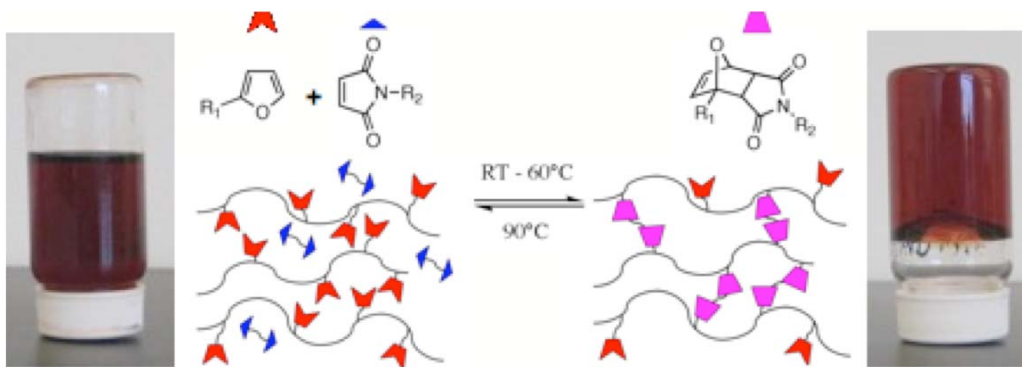
Materials that can repair cracks and recover from mechanical failure are desirable for a number of military applications. Because remendable materials both repair and prevent the propagation of cracks on the micro scale, they offer the potential for increased durability, safety, and cost efficiency for many applications. Two approaches for healing polymer networks have captured much attention. In one method, polymer networks are made to self-heal by adding microcapsules filled with uncured resin (Blaiszik et al. 2008; Brown et al. 2005; Kessler et al. 2003; Li et al. 2007; Liu et al. 2007; White et al. 2001; Yin et al. 2008). Upon fracture the microcapsules rupture releasing the resin, which hardens to heal the crack. The other method relies on the inherent reversibility of bonds designed into a polymer network (Bergman; Wudl 2008; Canary; Stevens 1992; Chen et al. 2002; Chujo et al. 1990; Cordier et al. 2008; Craven 1969; Fall; Ward 2001; Gheneim et al. 2002; Kalista; Ward 2007; Kavitha; Singha 2007; Kennedy; Castner 1979; Liu; Chen 2007; Liu et al. 2006; Murphy et al. 2008; Nijenhuis 1997; Salamone et al. 1988; Sijbesma 1997; Varley; van der Zwaag 2007). The reversible nature of these linkages allows for network remodeling at the

# Report Documentation Page

*Form Approved*  
*OMB No. 0704-0188*

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE <b>DEC 2008</b>	2. REPORT TYPE <b>N/A</b>	3. DATES COVERED <b>-</b>			
4. TITLE AND SUBTITLE <b>Remendable Polymeric Materials Using Reversible Covalent Bonds</b>		5a. CONTRACT NUMBER			
		5b. GRANT NUMBER			
		5c. PROGRAM ELEMENT NUMBER			
6. AUTHOR(S)		5d. PROJECT NUMBER			
		5e. TASK NUMBER			
		5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Drexel University, Department of Chemical &amp; Biological Engineering Philadelphia, PA 19104</b>		8. PERFORMING ORGANIZATION REPORT NUMBER			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)			
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)			
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release, distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>See also ADM002187. Proceedings of the Army Science Conference (26th) Held in Orlando, Florida on 1-4 December 2008, The original document contains color images.</b>					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>UU</b>	18. NUMBER OF PAGES <b>6</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			



**Figure 1.** Thermoreversible crosslinking gel: crosslinking chemistry (top center), a schematic of the reversible network (bottom center), and photographs showing liquid (left) and gel

damaged site. We have employed a composite approach to self-healing that combines many advantages of healing via encapsulation and healing via reversible bonds. This methodology allows for localized healing by including a secondary phase that induces healing through thermoreversible bonding while maintaining the mechanical and physical properties of the base thermoset.

We report on the development of two healing systems for epoxy-amine thermosets based on the thermoreversible Diels-Alder reaction of furan and maleimide. One system consists of a reversibly crosslinking network that can heal a traditional epoxy-amine thermoset. The ability to heal was evaluated by *in-situ* crack healing of modified compact tension (CT) specimens. In the other, furan functionalization of an epoxy-amine thermoset allows for bonding of this thermoset with a bismaleimide solution. Both systems heal at room temperature and minimal pressure. Additionally, significant load recovery is possible multiple times in a given location.

Healing with a secondary agent allows for crack healing while maintaining the desirable physical and mechanical properties of the base thermoset. Reversible bonding of the healing agent results in a material that exhibits the mobility of a linear polymer at increased temperatures and the mechanical properties of a crosslinked polymer at ambient conditions. The reversible healing agent also provides the ability to heal multiple times.

The Diels-Alder reaction is a cycloaddition of a diene and a dienophile. This reaction forms a ring structure at room temperature and reforms the respective diene (furan) and dienophile (maleimide) between 60 and 90°C.

## 2. MATERIALS

Furfuryl amine (FA), 1,1'-(methylenedi-4,1-phenylene)bismaleimide (BMI), furfuryl glycidyl ether

(FGE), phenyl glycidyl ether (PGE), and *N,N*-dimethylformamide DMF were obtained from Sigma-Aldrich. EPON 828, a Diglycidyl ether of bisphenol-A (DGEBA) with EEW=185-192 was obtained from Miller-Stephenson. 4,4'-methylenebis(cyclohexanamine) (PACM) was obtained from Air Products. All materials were used as received.

## 3. EXPERIMENTAL PROCEDURE

### 3.1 Synthesis of a Reversibly Crosslinking Gel

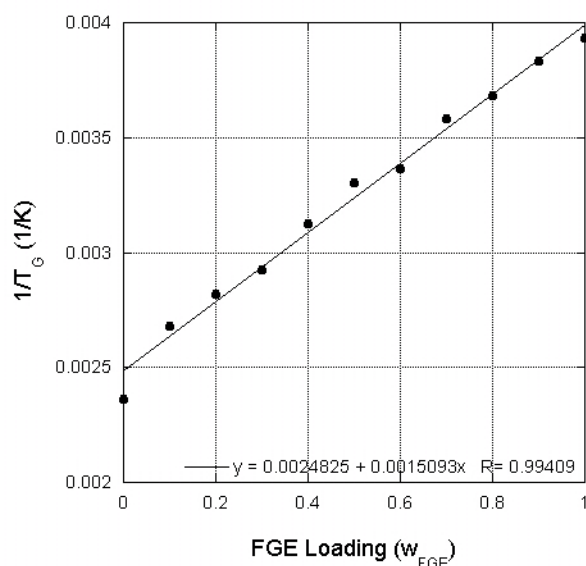
The crosslinks of this gel are based on the Diels-Alder reaction between maleimide groups on a bismaleimide and pendant furans on a linear polymer, similar to many other reversibly crosslinking networks (Craven 1969; Gheneim et al. 2002; Goiti et al. 2003; Gousse et al. 1998; Imai et al. 2000; Laita et al. 1997). A schematic representation of this network is shown in Figure 1 with maleimide moieties as triangles, furan moieties as notched trapezoids and Diels-Alder adducts as trapezoids. Also shown in Figure 1 are the Diels-Alder reaction and pictures of vials containing the liquid system at 90°C and the gel at room temperature (RT).

The linear polymer was a copolymer of FA and DGEBA. Stoichiometric amounts of FA and DGEBA were mixed to form a 15 wt.% solution in DMF which was reacted at 90°C for 30 hours. Crosslinking occurred by adding a stoichiometric amount of BMI to the linear polymer solution at room temperature and allowing sufficient time for reaction.

At room temperature the crosslinked network is a DMF-swollen gel. However, after approximately 20 minutes at 90°C a sufficient number of crosslinks are reversed so that the system liquifies and forms a polymer-bismaleimide solution in DMF. Upon cooling to ambient temperature a gel was observed to form after approximately 13 hours.

### 3.2 Synthesis of a Furan-Functionalized Network

Incorporation of furan groups in the polymer network was achieved through modification of an epoxy-amine network. DGEBA reacts via step growth polymerization with 4,4'-methylenebis(cyclohexyl) diamine (PACM), an aliphatic diamine. This system was modified by substituting DGEBA with a stoichiometric amount of furfuryl glycidyl ether (FGE), a furan-containing epoxy. In addition to providing furan functionality, the use of FGE as a comonomer allows for tailoring of  $T_g$ . The dependence of  $T_g$  on FGE loading is shown in Figure 2.  $T_g$  values were obtained from heating at a rate of  $10^\circ\text{C min}^{-1}$  with a TA Instruments Differential Scanning Calorimeter (DSC Q2000).



**Figure 2.**  $T_g$ -dependence on FGE content.

DGEBA, FGE, and PACM were mixed in stoichiometric amounts with a FGE loading of  $w_{FGE}=0.4$ , where  $w_{FGE}$  is the fraction by weight of epoxide groups contributed by FGE. The system was cured 2 hours at  $60^\circ\text{C}$  and 2 hours at  $90^\circ\text{C}$  to ensure complete cure. Full reaction was confirmed with DSC.

### 3.3 Compact Tension Testing

The reversibly crosslinked network was used as a healing agent for an epoxy-amine thermoset. The ability of the reversibly crosslinked gel to function as a healing agent was evaluated by measuring *in-situ* crack healing of modified CT specimens of DGEBA and PACM. DGEBA and PACM were mixed in stoichiometric amounts and cured for 2 hours at  $85^\circ\text{C}$  and 2 hours at  $165^\circ\text{C}$  to ensure complete cure and a  $T_g$  of  $160^\circ\text{C}$  (G. R. Palmese 1992). For comparison, base-line healing studies were also conducted with no healing agent, linear polymer solution in DMF, and pure DMF. Before injection into the crack, the healing agent (DMF, linear polymer solution, or

reversibly crosslinked polymer solution) was heated at  $90^\circ\text{C}$  for 1 hour.

Geometry and test procedure of CT specimens are explained in greater detail elsewhere (Chen et al. 2003). Specimens were loaded at a rate of  $0.1 \text{ mm min}^{-1}$  in tension until failure. Once CT specimens were fractured, the crack was filled with  $10 \mu\text{L}$  of healing agent and left to heal at room temperature under minimal pressure for 12 hours. After healing, specimens were loaded to failure to determine load recovery for heal 1. For subsequent healing cycles, specimens were heated at  $90^\circ\text{C}$  for 1 hour under no pressure, and healed for 12 hours at room temperature under minimal pressure. This testing procedure was repeated until specimens no longer recovered load following healing. Minimal pressure ( $\sim 4.7 \text{ kPa}$ ) during healing was provided by placing a 240 g plate on top of specimens.

## 4. RESULTS AND DISCUSSION

### 4.1 Crack Healing with Reversibly Crosslinked Network

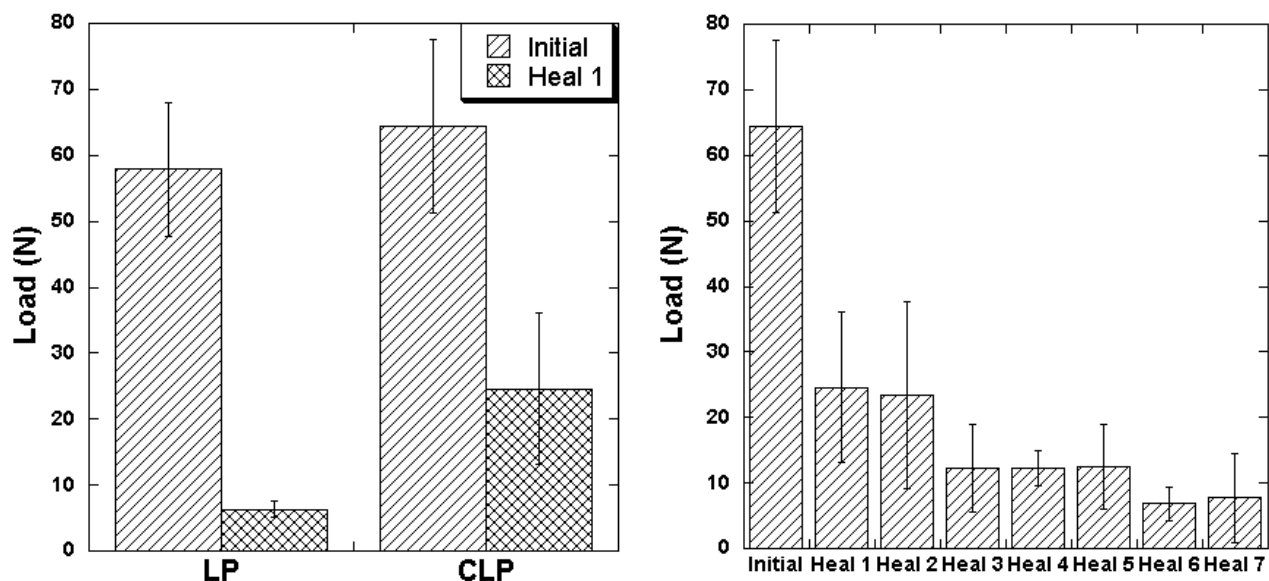
Results for load recovery are presented in Figure 3. Linear polymer and crosslinked polymer are labeled as LP and CLP, respectively. Healing values for DMF as the healing agent and systems with no healing agent are not shown because the specimens did not recover any load.

Load recoveries and healing efficiencies using the crosslinked polymer as a healing agent significantly outperform the linear polymer healing agent for the first heal. The linear polymer recovered an average load of  $6.3 \pm 1.2 \text{ N}$  ( $9.6 \pm 3.1\%$  healing efficiency), as compared to  $25 \pm 3.9 \text{ N}$  ( $37 \pm 8.3\%$ ) for the crosslinked polymer healing agent.

The inability of DMF to heal DGEBA-PACM runs counter to the work of Caruso et al. who observed solvent-promoted healing of another epoxy-amine network (Caruso et al. 2007). The difference in behavior could be due to the much higher crosslink density and  $T_g$  of our system.

### 4.2 Bonding with BMI Solutions

Specimens with  $w_{FGE}=0.4$  were polished using sandpaper of different grits and then “glued” together using  $\sim 0.02 \text{ g}$  of a high concentration BMI solution in DMF. Surface conditions play a significant role in healing. While specimens polished using 1600 grit sandpaper were bonded together effectively, specimens polished using 120 grit sandpaper did not adhere to one another. Additionally, specimens of a furan-free polymer network with the same crosslink density as  $w_{FGE}=0.4$  prepared with phenyl glycidyl ether (PGE), DGEBA, and



**Fig. 3** Load recovery for first heals for linear (LP) and crosslinked (CLP) healing agents (left) and subsequent heals for CLP (right). Error bars indicate standard deviations.

PACM did not bond using the BMI solution regardless of surface conditions. No system bonded when DMF was used as the glue.

We proposed that the primary healing mechanism is covalent bond formation across the crack surface. At room temperature furans and maleimides react via cycloaddition to form Diels-Alder adducts. In this system, BMI reacts with surface furans. If the distance between surfaces is less than the length of a BMI molecule, bonding can occur. Additional mechanisms, such as those related to the swelling behavior or  $T_g$  of the material may also play a role in healing.

## 5. CONCLUSIONS

We have developed a novel healing system based on the Diels-Alder reaction that allows a traditional epoxy-amine thermoset to recover mechanical properties multiple times following failure in the same location. In future work, methods of incorporating the thermoreversible gel into epoxy-amine thermosets will be investigated.

Future work in healing furan-functionalized networks will focus on characterizing healing using modified CT specimens as well as developing methods of incorporating BMI solutions in composites. Possibilities include hollow glass fibers and polymer microcapsules. Additionally, we plan to improve our understanding of the mechanisms of healing for this healing system so as to create materials with optimized healing abilities. Topics of interest include quantifying the effects of  $T_g$ , solvent, BMI concentration, and BMI structure on healing.

The literature contains many mentions of other furan-functionalized systems such as styrene, acrylics, and polyurethane (Canary; Stevens 1992; Craven 1969; Goiti et al. 2004; Gousse et al. 1998; Laita et al. 1997; Loy et al. 2002; Stevens 1979). Future work will include applying the Diels-Alder chemistry to non-epoxy networks and evaluating their healing ability.

## ACKNOWLEDGEMENTS

The authors wish to acknowledge the U.S. Army Research Laboratory for financial support under the Army Materials Center of Excellence Program, contract W911NF-06-2-0013 as well as the National Science Foundation for financial support under the Integrated Graduate Education and Research Traineeship in Nanoscale Science and Engineering administered by Drexel University and the University of Pennsylvania, contract DGE-0654313.

## REFERENCES

- Bergman, S., and F. Wudl, 2008: Mendable polymers. *J. Mater. Chem.*, **18**, 41.
- Blaiszik, B., N. R. Sottos, and S. R. White, 2008: Nanocapsules for self-healing materials. *Composites Science and Technology*, **68**, 978-986.
- Brown, E. N., S. R. White, and N. R. Sottos, 2005: Retardation and repair of fatigue cracks in a microcapsule toughened epoxy composite—Part II: In situ self-healing. *Composites Science and Technology*, **65**, 2474-2480.
- Canary, S. A., and M. Stevens, 1992: Thermally reversible crosslinking of polystyrene via the furan-maleimide Diels-Alder reaction. *J. Polym. Sci. A Polym. Chem.*, **30**, 1755-1760.
- Caruso, M. M., D. A. Delafuente, V. Ho, N. R. Sottos, J. Moore, and S. R. White, 2007: Solvent-Promoted Self-Healing Epoxy Materials. *Macromol. Rapid Commun.*
- Chen, X., F. Wudl, A. K. Mal, H. Shen, and S. R. Nutt, 2003: New Thermally Remendable Highly Cross-Linked Polymeric Materials. *Macromolecules*, **36**, 1802-1807.
- Chen, X., and Coauthors, 2002: A Thermally Remendable Cross-Linked Polymeric Material. *Science*, **295**, 1698-1702.
- Chujo, Y., K. Sada, and T. Saegusa, 1990: Reversible gelation of polyoxazoline by means of Diels-Alder reaction. *Macromolecules*, **23**, 2636-2641.
- Cordier, P., F. Tournilhac, C. Soulié-Ziakovic, and L. Leibler, 2008: Self-healing and thermoreversible rubber from supramolecular assembly. *Nature*, **451**, 977.
- Craven, J. M., 1969: Cross-linked Thermally Reversible Polymers Produced from Condensation Polymers with Pendant Furan Groups Cross-linked with Maleimides. *Patent*, **3,435,003**, 5.
- Fall, R., and T. Ward, 2001: Puncture Reversal of Ethylene Ionomers - Mechanistic Studies, Chemistry, 74 pp.
- G. R. Palmese, R. L. M., 1992: Effect of epoxy-amine stoichiometry on cured resin material properties. *Journal of Applied Polymer Science*, **46**, 1863-1873.
- Geng, X., 2005: Bismaleimide and Cyanate Ester Based Sequential Interpenetrating Polymer Networks for High Temperature Applications, Chemical Engineering, Drexel University, 221 pp.
- Gheneim, R., C. Perez-Berumen, and A. Gandini, 2002: Diels-Alder Reactions with Novel Polymeric Dienes and Dienophiles: Synthesis of Reversibly Cross-Linked Elastomers. *Macromolecules*, **35**, 7246-7253.
- Goiti, E., M. Huglin, and J. Rego, 2003: Thermal Breakdown by the Retro Diels-Alder Reaction of Crosslinking in Poly[styrene-co-(furfuryl methacrylate)]. *Macromol. Rapid Commun.*, **24**, 692-696.
- Goiti, E., M. Huglin, and J. M. Rego, 2004: Some properties of networks produced by the Diels-Alder reaction between poly(styrene-co-furfuryl methacrylate) and bismaleimide. *European Polymer Journal*, **40**, 219-226.
- Gousse, C., A. Gandini, and P. Hodge, 1998: Application of the Diels-Alder Reaction to Polymers Bearing Furan Moieties. 2. Diels-Alder and Retro-Diels-Alder Reactions Involving Furan Rings in Some Styrene Copolymers. *Macromolecules*, **31**, 314-321.
- Imai, Y., H. Itoh, K. Naka, and Y. Chujo, 2000: Thermally Reversible IPN Organic-Inorganic Polymer Hybrids Utilizing the Diels-Alder Reaction. *Macromolecules*, **33**, 4343-4346.
- Kalista, S. J., and T. C. Ward, 2007: Thermal characteristics of the self-healing response in poly(ethylene-co-methacrylic acid) copolymers. *Journal of The Royal Society Interface*, **4**, 405-411.
- Kavitha, A. A., and N. K. Singha, 2007: A tailor-made polymethacrylate bearing a reactive diene in reversible diels-alder reaction. *J. Polym. Sci. A Polym. Chem.*, **45**, 4441-4449.
- Kennedy, J. P., and K. F. Castner, 1979: Thermally reversible polymer systems by cyclopentadienylation. II. The synthesis of cyclopentadiene-containing polymers. *Journal of Polymer Science: Polymer Chemistry Edition*, **17**, 2055-2070.
- Kessler, M., N. R. Sottos, and S. R. White, 2003: Self-healing structural composite materials. *Composites Part A: Applied Science and Manufacturing*, **34**, 743-753.
- Laita, H., S. Boufi, and A. Gandini, 1997: The Application of the Diels-Alder Reaction to Polymers Bearing Furan Moieties 1. Reactions with Maleimides. *European Polymer Journal*, **33**, 1203.
- Li, H., R. Wang, X. He, W. Liu, and H. Hao, 2007: Preparation and characterization of self-healing poly (urea-formaldehyde) microcapsules. *International Conference on Smart Materials and Nanotechnology in Engineering. Edited by Du*, **6423**, 98.
- Liu, X., X. Sheng, J. K. Lee, and M. R. Kessler, 2007: Synthesis and characterization of melamine-urea-formaldehyde microcapsules containing ENB-based self-healing agents. *International Conference on Smart Materials and Nanotechnology in Engineering. Edited by Du*, **6423**, 112.
- Liu, Y., and Y. Chen, 2007: Thermally Reversible Cross-Linked Polyamides with High Toughness and Self-Repairing Ability from Maleimide- and Furan-Functionalized Aromatic Polyamides. *Macromolecular Chemistry and Physics*, **208**, 224-232.

- Liu, Y., C. Hsieh, and Y. Chen, 2006: Thermally reversible cross-linked polyamides and thermo-responsive gels by means of Diels–Alder reaction. *Polymer*, **47**, 2581-2586.
- Loy, D. A., D. R. Wheeler, J. R. Mcelhanon, and R. S. Saunders, 2002: Methods of making thermally removable polyurethanes. *Patent*, **6,403,753**, 13.
- Mcelhanon, J., and D. Wheeler, 2001: Thermally Responsive Dendrons and Dendrimers Based on Reversible Furan-Maleimide Diels–Alder Adducts . *Organic Letters*, **3**, 2681-2683.
- Murphy, E. B., E. Bolanos, C. Schaffner-Hamann, F. Wudl, S. R. Nutt, and M. L. Auad, 2008: Synthesis and Characterization of a Single-Component Thermally Remendable Polymer Network: Staudinger and Stille Revisited. *Macromolecules*, **41**, 3169-3174.
- Nijenhuis, K., 1997: Thermoreversible Networks. *Advances in Polymer Science*, **130**, 51-57.
- Raman, V. I., and G. R. Palmese, 2005: Influence of Tetrahydrofuran on Epoxy-Amine Polymerization. *Macromolecules*, **38**, 6923-6930.
- Salamone, J. C., Y. Chung, S. B. Clough, and A. C. Watterson, 1988: Thermally reversible, covalently crosslinked polyphosphazenes. *Journal of Polymer Science Part A: Polymer Chemistry*, **26**, 2923-2939.
- Sijbesma, R., 1997: Reversible Polymers Formed from Self-Complementary Monomers Using Quadruple Hydrogen Bonding. *Science*, **278**, 1601-1604.
- Stevens, M. P., 1979: Crosslinking of polystyrene via pendant maleimide groups. *J. Polym. Sci. A Polym. Chem.*, **17**, 3675-3685.
- Varley, R., and S. van der Zwaag, 2007: Ionomers as Self Healing Polymers. *Self Healing Materials*, 95-114.
- White, S. R., and Coauthors, 2001: Autonomic healing of polymer composites. *Nature*, **409**, 794-797.
- Yin, T., L. Zhou, M. Zhi Rong, and M. Qiu Zhang, 2008: Self-healing woven glass fabric/epoxy composites with the healant consisting of micro-encapsulated epoxy and latent curing agent. *Smart Mater. Struct.*, **17**, 5019.