JOURNAL OF THE ROYAL SOCIETY Interface

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J. R. Soc. Interface 2007 **4**, 359-362
doi: 10.1098/rsif.2006.0202

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doi:10.1098/rsif.2006.0202

Towards electrically conductive, self-healing materials

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A novel class of organometallic polymers comprising *N*-heterocyclic carbenes and transition metals was shown to have potential as an electrically conductive, self-healing material. These polymers were found to exhibit conductivities of the order of $10^{-3}\ \mathrm{S\,cm^{-1}}$ and showed structurally dynamic characteristics in the solid-state. Thin films of these materials were cast onto silicon wafers, then scored and imaged using a scanning electron microscopy (SEM). The scored films were subsequently healed via thermal treatment, which enabled the material to flow via a unique depolymerization process, as determined by SEM and surface profilometry. A method for incorporating these features into a device that exhibits electrically driven, self-healing functions is proposed.

Keywords: self-healing materials; *N*-heterocyclic carbenes; organometallic polymers; electrically conductive materials

1. INTRODUCTION

The formation and propagation of microcracks caused by exposure to continuous and/or cyclic stress is a main culprit of fatigue in mechanical materials and failure in electronic components (Sauer & Hara 1990). Cutting-edge research has focused on addressing this problem through the development of responsive materials with ‘self-healing’ capabilities. Prime examples include epoxy-based composites containing encapsulated healing agents (Kessler & White 2001; White *et al.* 2001; Rule *et al.* 2005) and thermally remendable plastics comprising monomers that reversibly conjoin (Chen *et al.* 2002, 2003). Despite these brilliant advances, self-healing materials have yet to reach their full potential. For example, the aforementioned examples are inherently electrically insulating, which limits their ultimate responsivities and precludes their use in related analytical applications. By imparting conductive properties into these materials, a number of unique and useful features may be realized. For example, one may obtain ‘real-time’ status of a material’s structural integrity through electronic feedback mechanisms. This feature could lead to new approaches for detecting and quantifying microcracks (an extremely challenging task), which, in turn, could lead to materials capable of recording their stress/load histories. Other possibilities include using electric fields or currents as novel healing functions (an example of an ‘electrically driven self-healing’ process will be described in §2). While materials exhibiting both self-healing and conductive properties can be expected to offer obvious advantages in omnipresent consumer electronics, they may also provide practical alternatives to sophisticated redundancy and other types of back-up systems currently used for high-risk situations, such as deep-sea and space travel.

2. RESULTS AND DISCUSSION

A number of approaches may be envisioned to impart conductive properties into self-healing materials. For example, composites of the aforementioned responsive materials with self-healing capabilities can be synthesized with metals, alloys, nanoparticles and other types of electrical conductors. However, this is likely to result in long-standing phase compatibility and processability issues associated with these latter materials. We desired a *de novo* solution that tackled this problem from the ‘ground up’, i.e. from a molecular level. We sought a means to construct a stimulus–responsive material that effectively combined structurally dynamic characteristics with electrically conductive properties. Figure 1 shows a generalized depiction of how a material with such features may operate if used as an electrical wire or incorporated into a device. Upon the formation of a microcrack, the total number of electron percolation pathways within the material should decrease. As a result, its inherent electrical resistance should increase accordingly. If the material is integrated into a circuit containing an ammeter/voltmeter, then the drop in conductivity could be used to trigger a simultaneous increase in the applied electric field. Considering that the microcrack is the source of the increased resistance, this voltage bias should result in the generation of heat localized at the microcrack. By harnessing the generated thermal energy to hurdle kinetic barriers, the system may be

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One contribution of 9 to a themed supplement ‘Self-healing polymers and composites’.

Received 27 September 2006
Accepted 28 November 2006

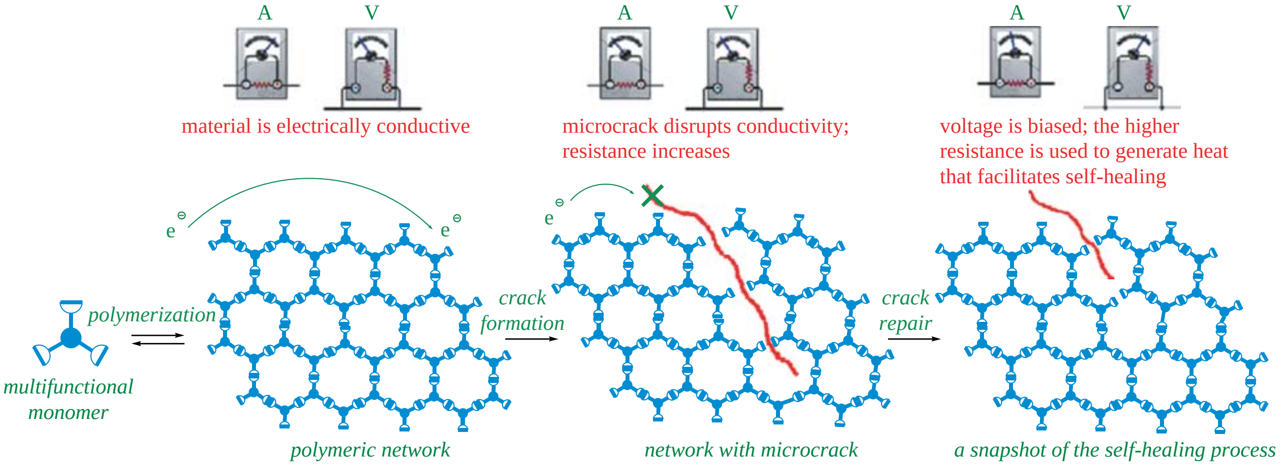
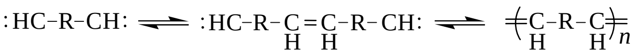


Figure 1. Operation of an electrically conductive, self-healing material. A, amperes; V, volts.



$$:\mathrm{HC{-}R{-}CH}: \rightleftharpoons :\mathrm{HC{-}R{-}}\underset{\mathrm{H}}{\mathrm{C}}=\underset{\mathrm{H}}{\mathrm{C}}\mathrm{{-}R{-}CH}: \rightleftharpoons \left(\underset{\mathrm{H}}{\mathrm{C}}\mathrm{{-}R{-}}\underset{\mathrm{H}}{\mathrm{C}}\right)_n$$

Figure 2. A hypothetical polymerization where unsaturation is maintained as a monomer is converted to a polymer (R, unsaturated linker).

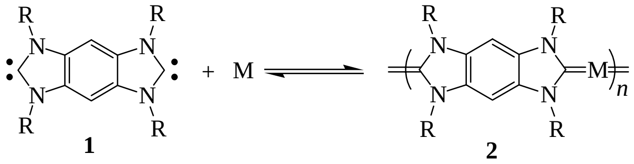


Figure 3. A dynamic equilibrium between a monomer species (left) and a organometallic polymer (right) that is controlled via an external stimulus, such as heat.

electrically driven back to its original (i.e. a low-resistance/high-current) state.

In order to realize the previously described system, the development of a new responsive polymeric material with the following features was needed: (i) the material must be electrically conductive, (ii) the polymerization process must be dynamic and responsive to changes in external stimuli, (iii) for practical reasons, the polymerization process should also exhibit high atom economy (i.e. no by-product evolution), (iv) bond scission (i.e. depolymerization) should occur only in the vicinity of the microcrack (Wool & O'Connor 1981; Kim & Wool 1983), and (v) main-chain unsaturation, a key requirement for conductivity, must be conserved or increased upon polymerization (figure 2). In addition, modular components were desired to facilitate systematic tuning of material and electronic properties.

Although an impressive range of dynamic polymerizations is known, the fundamental reversible reactions involved do not meet the conductivity requirement (Bell *et al.* 2002; Rowan *et al.* 2002; Otsuka *et al.* 2003; Chung *et al.* 2004; Skene & Lehn 2004; Kolomiets & Lehn 2005; Ono *et al.* 2005; Scott *et al.* 2005). One exception are complexes formed between *N*-heterocyclic carbenes (NHCs) and transition metals. These are not only known to form reversibly with tunable equilibrium constants, but also their electronic communications within these systems are well studied (Lewis *et al.* 2003; Scott & Nolan 2005). Implementation of these complexes in polymeric materials required the synthesis of appropriately functionalized multitopic NHCs (**1**) poised for polymerization. Through a series of synthetic developments, we successfully prepared such NHCs and demonstrated that they may be combined with group X metal salts to provide well-defined organometallic polymers (**2**; M=Ni, Pd and Pt; R=alkyl, benzyl and aryl; figure 3; Boydston *et al.* 2005, 2006; Khramov *et al.* 2006*a*,*b*; Boydston & Bielawski 2006). After these polymers were found to be structurally dynamic, efforts were directed towards evaluating their electronic properties. Conductivities of polymeric films are typically measured using a four-point probe technique, which accounts for contact resistances between the polymer film and the gold contacts, as well as resistances between the contacts and the electrodes. In this method, four equidistant gold contacts are first deposited in a linear arrangement on the film. Current is then applied from an outer electrode and electrical potential distribution is measured between the inner two electrodes. Applying this technique to (undoped) 700 nm films of **2** resulted in conductivities of the order of 10^{-3} S cm^{-1}. For comparison, Si, a metalloid used in the semiconductor industry, exhibits a conductivity of the order of 10^{-5} S cm^{-1}.

The potential of these materials in self-healing applications was investigated using a scanning electron microscopy (SEM). Gold deposition was found to be unnecessary to obtain visible images of these materials, a testament of their high conductivities, which provided a unique opportunity to visualize any healing processes. Cross-linked thin films (800 nm) were first cast on silicon wafers and, to emulate microcrack formation, a sharp razor blade was used to score the films. After imaging (figure 4*a*), the material was then heated at 200°C for 25 min, allowed to cool and then re-imaged (figure 4*b*). Comparing these images clearly indicated that rough edges introduced by the razor blade were visibly smoothened upon thermal treatment. Encouraged by this result, and in conjunction with the fact that the dynamic behaviour of the system had been established in solution, it was predicted that the presence of a solvent might facilitate the reformation of the broken NHC–metal bonds.

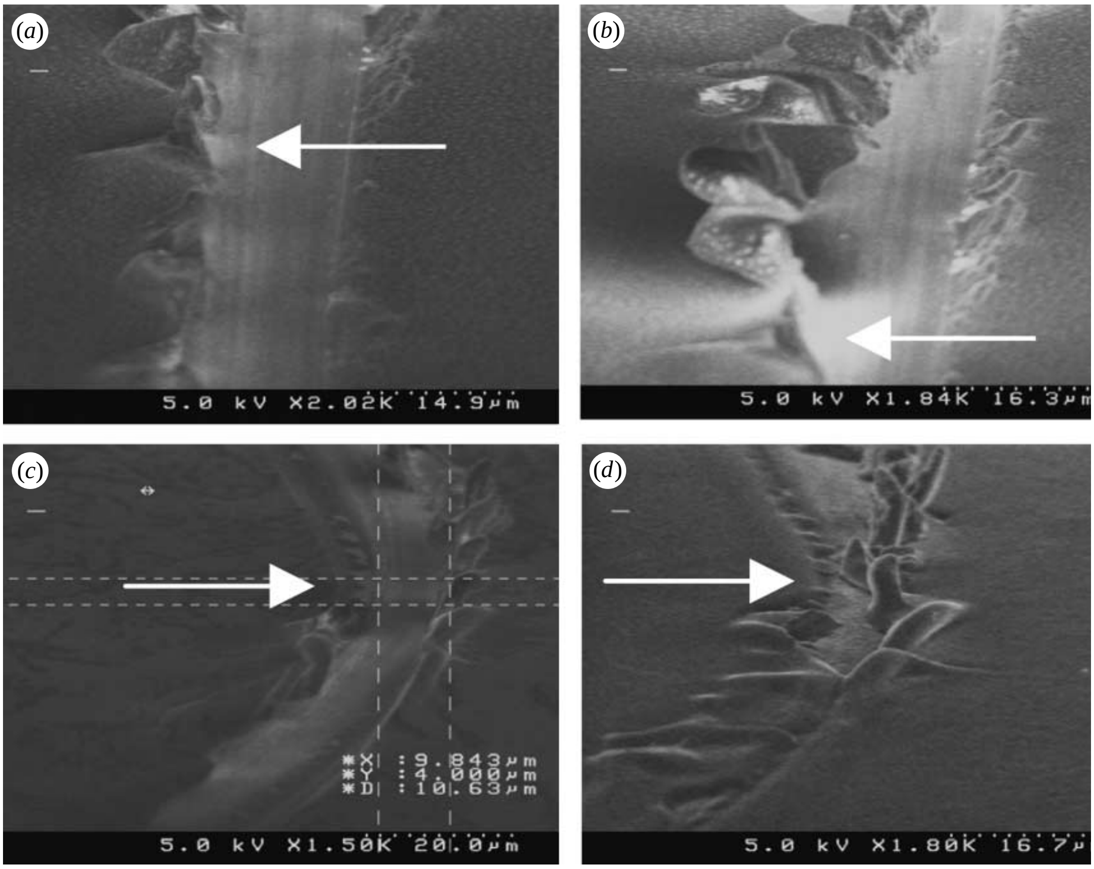


Figure 4. The scanning electron micrographs of a scored organometallic polymer film (*a*) before and (*b*) after exposure to 200°C for 15 min, and (*c*) before and (*d*) after exposure to 150°C for 2 h in the presence of DMSO vapour. Arrows indicate a common point of reference.

Towards this end, a thin film of the material was cast on a silicon wafer, and a crack was introduced and imaged as before (figure 4*c*). The wafer was then heated at 150°C for 2 h in a compartmentalized sealed vessel. A pool of dimethylsulphoxide (DMSO) was placed in a contiguous compartment, so that the solvent vapour would facilitate healing. Comparison of the SEM image of the treated film (figure 4*d*) indicated that the razor-induced crack was now refilled with the material. This observation was supported by measuring the film's surface with a stylus profiler, which indicated that the depth of the crack had been significantly reduced (from 800 nm to nearly 0 nm) in the healed films. We are currently assessing the extent to which microcracks and self-healing efficiencies can be quantified by this unique combination of characterization techniques.

3. CONCLUSIONS

Collectively, these results suggest that self-healing characteristics were observed in materials with electrically conductive properties. However, many challenges remain before their potential is fully realized. Most importantly, their dependency on solvent vapour to facilitate healing must be eliminated. Incorporating bulky *N*-alkyl groups, such as 2,2-dimethylbutyl, into the carbene moieties should frustrate crystallization, reduce the viscosities of the respective polymers and help the material 'flow' into neighbouring microcracks upon depolymerization.

Additionally, the electronic performance of these materials must be enhanced to more than or equal to 1 S cm^{-1} in order for them to be broadly useful. This may be achieved by properly matching the reduction–oxidation potentials of the transition metal with the *N*-heterocyclic carbene, a well-known method for maximizing electronic communication in organometallic materials (Holliday & Swager 2005). Efforts towards these goals, as well as exploring the potential of deploying these materials in many of the aforementioned applications, are currently underway.

We are grateful to the US Army Research Office (W911NF-05-1-0430), the Welch Foundation (F-1621), the Petroleum Research Fund, as administered by the American Chemical Society (44071-G1), and The University of Texas at Austin for their generous financial support. A.J.B. thanks UT-Austin for a University Continuing Fellowship.

REFERENCES

Bell, S. A., Meyer, T. Y. & Geib, S. J. 2002 Catalytic double-bond metathesis without the transition metal. *J. Am. Chem. Soc.* **124**, 10 698–10 705. (doi:10.1021/ja020494v)

Boydston, A. J. & Bielawski, C. W. 2006 Bis(imidazolylidene)s as modular building blocks for monomeric and macromolecular organometallic materials. *Dalton Trans.* **35**, 4073–4077. (doi:10.1039/b607696n)

Boydston, A. J., Williams, K. A. & Bielawski, C. W. 2005 A modular approach to main-chain organometallic polymers. *J. Am. Chem. Soc.* **127**, 12 496–12 497. (doi:10.1021/ja054029k)

Boydston, A. J., Khramov, D. M. & Bielawski, C. W. 2006 An alternative synthesis of benzobis(imidazolium) salts via a 'one-pot' cyclization/oxidation reaction sequence. *Tetrahedron Lett.* **47**, 5123–5125. (doi:10.1016/j.tetlet.2006.05.076)

Chen, X., Dam, M. A., Ono, K., Mal, A., Shen, H., Nutt, S. R., Sheran, K. & Wudl, F. 2002 A thermally re-mendable cross-linked polymeric material. *Science* **295**, 1698–1702. (doi:10.1126/science.1065879)

Chen, X., Wudl, F., Mal, A., Shen, H. & Nut, S. R. 2003 New thermally remendable highly cross-linked polymeric material. *Macromolecules* **36**, 1802–1807. (doi:10.1021/ma0210675)

Chung, C.-M., Roh, Y. S., Cho, S.-Y. & Kim, J.-G. 2004 Crack healing in polymeric materials via photochemical [2+2] cycloaddition. *Chem. Mater.* **16**, 3982–3984. (doi:10.1021/cm049394+)

Holliday, B. J. & Swager, T. M. 2005 Conducting metallopolymers: the roles of molecular architecture and redox matching. *Chem. Commun.* **41**, 23–36. (doi:10.1039/b408479a)

Kessler, M. R. & White, S. R. 2001 Self-activated healing of delamination damage in woven composites. *Composites A* **32**, 683–699. (doi:10.1016/S1359-835X(00)00149-4)

Khramov, D. M., Boydston, A. J. & Bielawski, C. W. 2006*a* Highly efficient synthesis and solid-state characterization of 1,2,4,5-tetrakis(alkyl- and arylamino)benzenes and cyclization to their respective benzobis(imidazolium) salts. *Org. Lett.* **8**, 1831–1834. (doi:10.1021/ol060349c)

Khramov, D. M., Boydston, A. J. & Bielawski, C. W. 2006*b* Synthesis and study of janus bis(carbene)s and their transition-metal complexes. *Angew. Chem. Int. Ed.* **45**, 6186–6189. (doi:10.1002/anie.200601583)

Kim, Y. H. & Wool, R. P. 1983 A theory of healing at a polymer-polymer interface. *Macromolecules* **16**, 1115–1120. (doi:10.1021/ma00241a013)

Kolomiets, B. & Lehn, J.-M. 2005 Double dynamers: molecular and supramolecular double dynamic polymers. *Chem. Commun.* **41**, 1519–1521. (doi:10.1039/b418899c)

Lewis, A. K. de K., Caddick, S., Cloke, F. G. N., Billingham, N. C., Hitchcock, P. B. & Leonard, J. 2003 Synthetic, structural, and mechanistic studies on the oxidative addition of aromatic chlorides to a palladium (*N*-heterocyclic carbene) complex: relevance to catalytic amination. *J. Am. Chem. Soc.* **125**, 10 066–10 073. (doi:10.1021/ja035565k)

Ono, T., Nobori, T. & Lehn, J.-M. 2005 Dynamic polymer blends—component recombination between neat dynamic covalent polymers at room temperature. *Chem. Commun.* **41**, 1522–1524. (doi:10.1039/b418967a)

Otsuka, H., Aotani, K., Higaki, Y. & Takahara, A. 2003 Polymer scrambling: macromolecular radical crossover reaction between the main chains of alkoxyamine-based dynamic covalent polymers. *J. Am. Chem. Soc.* **125**, 4064–4065. (doi:10.1021/ja0340477)

Rowan, S. J., Cantrill, S. J., Cousins, G. R. L., Sanders, J. K. M. & Stoddart, J. F. 2002 Dynamic covalent chemistry. *Angew. Chem. Int. Ed.* **41**, 898–952. (doi:10.1002/1521-3773(20020315)41:6<898::AID-ANIE898>3.0.CO;2-E)

Rule, J. D., Brown, E. N., Sottos, N. R., White, S. R. & Moore, J. S. 2005 Wax protected catalyst microspheres for efficient self-healing materials. *Adv. Mater.* **17**, 205–208. (doi:10.1002/adma.200400607)

Sauer, J. A. & Hara, M. 1990 Effect of molecular variables on crazing and fatigue of polymers. *Adv. Polym. Sci.* **91/92**, 69–118. (doi:10.1007/BFb0018019)

Scott, N. M. & Nolan, S. P. 2005 Stabilization of organic species achieved by the use of N-heterocyclic carbene (NHC) ligands. *Eur. J. Inorg. Chem.*, 1815–1828. (doi:10.1002/ejic.200500030)

Scott, T. F., Schneider, A. D., Cook, W. D. & Bowman, C. N. 2005 Photoinduced plasticity in cross-linked polymers. *Science* **308**, 1615–1617. (doi:10.1126/science.1110505)

Skene, W. G. & Lehn, J.-M. 2004 Dynamers: polyacylhydrazone reversible covalent polymers, component exchange, and constitutional diversity. *Proc. Natl Acad. Sci. USA* **101**, 8270–8275. (doi:10.1073/pnas.0401885101)

White, S. R., Sottos, N. R., Geubelle, P. H., Moore, J. S., Kessler, M. R., Sriram, S. R., Brown, E. N. & Viswanathan, S. 2001 Autonomic healing of polymer composites. *Nature* **409**, 794–797. (doi:10.1038/35057232)

Wool, R. P. & O'Connor, K. M. 1981 A theory of crack healing in polymers. *J. Appl. Phys.* **52**, 5953–5963. (doi:10.1063/1.328526)