This is a repository copy of A mechanically and electrically self-healing graphite composite dough for stencil-printable stretchable conductors.

White Rose Research Online URL for this paper: http://eprints.whiterose.ac.uk/99078/

Version: Accepted Version

**Article:**

https://doi.org/10.1039/C6TC01052K

---

**Reuse**
Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

**Takedown**
If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.
This article can be cited before page numbers have been issued, to do this please use: T. Wu and B. Chen, J. Mater. Chem. C, 2016, DOI: 10.1039/C6TC01052K.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
A composite dough composed of a liquid polymer with embedded graphite was reported, showing rapid mechanical and electrical self-healing properties at ambient conditions. The study demonstrated the composite could be used as highly stretchable electrical conductor with desirable characteristics, such as stable electrical restoration during repeated stretching cycles and touch-healing of disconnections.

Stretchable electronic devices are of importance in prosthetics and the emerging field of soft robotics, which have motivated intensive efforts in many areas, including large-area electronic displays, sensors, actuators, energy storage/generation devices and implantable devices for health monitoring. These earlier studies have revealed that stretchable conductors are essential components in stretchable electronics. The stretchability of conductors largely depends on the properties of conducting materials and their fabrication on elastomeric substrates. Due to the rigid nature of conventional conducting materials, their flexibility is always limited in comparison with the elastomeric substrates. Some irreversible mechanical damages/cracks in conducting materials are inevitable during repeated deformations, especially under larger strains. Therefore, restoration of the conductivity of electronic components after ruptures without an external aid could be of great significance for building advanced stretchable conductors.

Inspired by the self-healing ability of the skins from mankind and animals, self-healing conductors are receiving growing attention, especially in a number of advanced electronic fields, such as supercapacitors, lithium-ion batteries, thermal sensors, chemical sensors, and electronic skin. Self-healing chemistry is of great technological interest, because the self-healing feature is expected to not only enhance the product lifetime and durability, but also open new opportunities in many fields. However, the integration of intrinsic self-healing and functional capabilities remains a challenge for stretchable conductors. Several approaches have been reported towards building intrinsic, room-temperature self-healing conductors. One is using capsule-releasing techniques containing conducting fluids, which are not repeatable once capsules exhausted. Another is the combination of supramolecular elastomers with conducting fillers. The association/dissociation of reversible bonds (e.g. dynamic covalent or physical bonds) of the elastomers provide the healing mechanism in this type of composites. The self-healing elastomer can act multiple times, providing repeatable recovery of mechanical and electrical properties. Lately, Oh and coworkers reported another approach using an intrinsically viscoelastic dough of conducting polymer which can flow and repair the defect areas.

Carbon-based materials (such as one-dimensional carbon nanotubes and two-dimensional graphene nanosheets) have recently caused intense research interests in flexible and conductive polymer composites due to their unique electronic structures and mechanical properties. Herein, we report a facile method to prepare a robust, electrically conductive graphite/polymer composite dough able to mechanically and electrically self-heal at ambient conditions. A relatively high conductivity of 1.98 S cm\(^{-1}\) was measured for our composite dough. The composite dough could be easily processed and used either as bulk material or in film form. The stretchable conductor based on the composite dough could almost fully restore its conductivity after multiple damages.

Branchied polyethylenimine (bPEI) is a room-temperature liquid polymer which is rich of various amine groups (i.e. primary, secondary and tertiary amines). As shown in Fig. 1a, bPEI exhibits a well-defined predominantly viscous behavior (the loss modulus \(G'\) dominating the storage modulus \(G'\)) in the range of frequencies analyzed. The graphite/bPEI composite dough is composed of 65 wt% graphite and 35 wt% bPEI, where the volume content of graphite (48 vol% as calculated in ESI ) is close to the upper bound of the percolation threshold range for 3D randomly distributed graphite platelets (50 vol%) to ensure the formation of a graphite network in the composite. The graphite network acts as a continuous electrical path providing electrical conductivity up to 1.98 ± 0.17 S cm\(^{-1}\) as measured, which is more than two times the...
value for the self-healing polyborosiloxane composite based on reduced graphene oxide scaffold (0.9 S cm$^{-1}$). The graphite network also acts as a skeleton that confines bPEI, impeding its flow, which likely reduces the segment relaxation of bPEI, thus leading to a $G'$ around five orders of magnitude of the value for bPEI alone at lower frequencies. Moreover, a change to the rheological response is found, from Newtonian behavior of bPEI alone to shear-thinning behavior of graphite/bPEI, due to the presence of a fragile graphite skeleton, which is in agreement with other filled polymeric systems with relatively high filler additions. More importantly, with such a high addition, graphite/bPEI maintains the fluid-like behavior ($G'' > G'$) at higher frequencies, which will boost its moldability/formability during the preparation of stretchable conductors. The previous atomic force microscopy study on the adsorption of bPEI on graphite in aqueous solution has confirmed the attractive specific interaction (the dipolar interaction) between bPEI and graphite. The nanometer-scale corrugated surface of graphite provides an adequate surface area for bPEI wetting. Fig. 1b shows a good wettablility of bPEI on the surface of graphite, which leads to a reduction in phase aggregation and a relatively uniform dispersion of graphite in bPEI. The compressive modulus of graphite/bPEI is measured as 0.2 ± 0.04 MPa (Fig. S1 in ESI). Graphite/bPEI is self-supporting, showing no spontaneous flow under its own gravity and being able to remain its given shape (Fig. 1c). Similar phenomena were widely observed in other viscoelastic materials, like clay paste and toothpaste, needing a critical shear stress for fluidic deformation.

The composite dough is able to mechanically self-heal after fracture (Fig. 1d) and self-adhere to substrates (without the use of adhesives) such as stretchable thermoplastic polyurethane (TPU) sheets used in this study. Fig. 1e shows a representative stress–strain curves of graphite/bPEI original and healed samples. To investigate the mechanical healing of graphite/bPEI, the composite dough was completely bifurcated using a scalpel and the two fractured surfaces were brought together by applying a gentle pressure (~1 kPa) for 2 s and then released to allow recovering for another 8 s. The mechanical healing efficiency is quantified using toughness (the area under strain-stress curve up to fracture), defined as the proportion of toughness restored relative to the original toughness according to the previous work. From these curves, the healing efficiency was calculated to be 59% after a total healing duration of 10 s. This self-healing ability remained nearly constant even after the two fracture surfaces were kept apart for 48 h before self-healing (Fig. S2). The reversible physical interactions in the composite dough, including the multiple hydrogen bonding of bPEI and the attractive dipolar interaction between bPEI and graphite, can break preferentially during a mechanical damage event and associate dynamically at the fracture surface during a healing process, which provides the self-healing mechanism at ambient conditions. It was also found that the healing efficiency could be increased in an environment with a higher relative humidity, e.g. to 72% for a humidity of 100% (Fig. S3). This might be because the mobility of bPEI chains was improved by hydration, which benefits the diffusion of the chains and association of hydrogen bonds between the two fracture surfaces. It is noteworthy that a gentle pressure applied to push the fracture surface of two halves of graphite/bPEI together is necessary for the self-healing due to its viscoelastic properties as described above.

This requirement also applies to other advanced self-healing composites.
The resistance stably recovers its initial value during repeated stretching cycles with a fixed strain up to 100% (Fig. 3b). The conductive recovering efficiency was measured at 96% even after five stretching cycles. This is because the overall mechanical behavior of graphite/bPEI is governed by the mechanical cycles of the elastomer substrate. Electrical conductivity of graphite/bPEI is attributed to the physical networks of graphite. When strains are beyond 50%, graphite networks will be gradually destroyed, leading to the significant increase in resistance. With the assistance of the resilience force of elastomeric substrate, graphite/bPEI can repair their physical networks completely and so electrical conductivity as well. This is expected to be an advantage of self-healing conducting materials when used in stretchable electronics. Fig. 3c exhibits the deformability of graphite/bPEI/TPU conductor in extreme motions such as stretching and twisting. The LED had negligible degradation in light intensity during repeated motions confirming the stretchability and flexibility of the device. In the case that the damage of graphite/bPEI occurs with the absence of the resilience force, only a gentle external pressure like finger touch (~1.5 kPa) is necessary to repair the conductor. Fig. 4a displays the lighting experiment during cutting-off and touch-healing of graphite/bPEI/TPU conductor. After cutting off graphite/bPEI, the electrical disconnection was maintained because of the viscoelastic property of graphite/bPEI as described above; however, the current immediately recovered its initial value after a gentle finger touch. The finger touch made the composite flow into the damaged area. This rapid, stable touch-healing was highly reproducible shown in Fig. 4b. The conductive touch-healing efficiency was measured at 95% after five cuts.

The conducting graphite/bPEI composite dough could self-adhere to elastomer substrates, which is highly useful in fabricating stretchable conductors. A graphite/bPEI/TPU conductor was constructed by stenciling a 100-μm-thick graphite/bPEI layer on a TPU substrate. The change in resistance of the conductor is plotted as a function of strain with error bars (standard deviation) in Fig. 3a. The resistance shows only a small increase as the strain increased up to 50% (namely, a 25% loss in conductance) and a rapid rise afterward. This basically matches the stretching and contraction strains of up to 55% generated by the movements of human joints. The resistance stably recovers its initial value during repeated stretching cycles with a fixed strain up to 100% (Fig. 3b). The conductive recovering efficiency was measured at 96% even after five stretching cycles. This is because the overall mechanical behavior of graphite/bPEI is governed by the mechanical cycles of the elastomer substrate. Electrical conductivity of graphite/bPEI is attributed to the physical networks of graphite. When strains are beyond 50%, graphite networks will be gradually destroyed, leading to the significant increase in resistance. With the assistance of the resilience force of elastomeric substrate, graphite/bPEI can repair their physical networks completely and so electrical conductivity as well. This is expected to be an advantage of self-healing conducting materials when used in stretchable electronics. Fig. 3c exhibits the deformability of graphite/bPEI/TPU conductor in extreme motions such as stretching and twisting. The LED had negligible degradation in light intensity during repeated motions confirming the stretchability and flexibility of the device. In the case that the damage of graphite/bPEI occurs with the absence of the resilience force, only a gentle external pressure like finger touch (~1.5 kPa) is necessary to repair the conductor. Fig. 4a displays the lighting experiment during cutting-off and touch-healing of graphite/bPEI/TPU conductor. After cutting off graphite/bPEI, the electrical disconnection was maintained because of the viscoelastic property of graphite/bPEI as described above; however, the current immediately recovered its initial value after a gentle finger touch. The finger touch made the composite flow into the damaged area. This rapid, stable touch-healing was highly reproducible shown in Fig. 4b. The conductive touch-healing efficiency was measured at 95% after five cuts.

The resistance stably recovers its initial value during repeated stretching cycles with a fixed strain up to 100% (Fig. 3b). The conductive recovering efficiency was measured at 96% even after five stretching cycles. This is because the overall mechanical behavior of graphite/bPEI is governed by the mechanical cycles of the elastomer substrate. Electrical conductivity of graphite/bPEI is attributed to the physical networks of graphite. When strains are beyond 50%, graphite networks will be gradually destroyed, leading to the significant increase in resistance. With the assistance of the resilience force of elastomeric substrate, graphite/bPEI can repair their physical networks completely and so electrical conductivity as well. This is expected to be an advantage of self-healing conducting materials when used in stretchable electronics. Fig. 3c exhibits the deformability of graphite/bPEI/TPU conductor in extreme motions such as stretching and twisting. The LED had negligible degradation in light intensity during repeated motions confirming the stretchability and flexibility of the device. In the case that the damage of graphite/bPEI occurs with the absence of the resilience force, only a gentle external pressure like finger touch (~1.5 kPa) is necessary to repair the conductor. Fig. 4a displays the lighting experiment during cutting-off and touch-healing of graphite/bPEI/TPU conductor. After cutting off graphite/bPEI, the electrical disconnection was maintained because of the viscoelastic property of graphite/bPEI as described above; however, the current immediately recovered its initial value after a gentle finger touch. The finger touch made the composite flow into the damaged area. This rapid, stable touch-healing was highly reproducible shown in Fig. 4b. The conductive touch-healing efficiency was measured at 95% after five cuts.

The conducting graphite/bPEI composite dough could self-adhere to elastomer substrates, which is highly useful in fabricating stretchable conductors. A graphite/bPEI/TPU conductor was constructed by stenciling a 100-μm-thick graphite/bPEI layer on a TPU substrate. The change in resistance of the conductor is plotted as a function of strain with error bars (standard deviation) in Fig. 3a. The resistance shows only a small increase as the strain increased up to 50% (namely, a 25% loss in conductance) and a rapid rise afterward. This basically matches the stretching and contraction strains of up to 55% generated by the movements of human joints. The resistance stably recovers its initial value during repeated stretching cycles with a fixed strain up to 100% (Fig. 3b). The conductive recovering efficiency was measured at 96% even after five stretching cycles. This is because the overall mechanical behavior of graphite/bPEI is governed by the mechanical cycles of the elastomer substrate. Electrical conductivity of graphite/bPEI is attributed to the physical networks of graphite. When strains are beyond 50%, graphite networks will be gradually destroyed, leading to the significant increase in resistance. With the assistance of the resilience force of elastomeric substrate, graphite/bPEI can repair their physical networks completely and so electrical conductivity as well. This is expected to be an advantage of self-healing conducting materials when used in stretchable electronics. Fig. 3c exhibits the deformability of graphite/bPEI/TPU conductor in extreme motions such as stretching and twisting. The LED had negligible degradation in light intensity during repeated motions confirming the stretchability and flexibility of the device. In the case that the damage of graphite/bPEI occurs with the absence of the resilience force, only a gentle external pressure like finger touch (~1.5 kPa) is necessary to repair the conductor. Fig. 4a displays the lighting experiment during cutting-off and touch-healing of graphite/bPEI/TPU conductor. After cutting off graphite/bPEI, the electrical disconnection was maintained because of the viscoelastic property of graphite/bPEI as described above; however, the current immediately recovered its initial value after a gentle finger touch. The finger touch made the composite flow into the damaged area. This rapid, stable touch-healing was highly reproducible shown in Fig. 4b. The conductive touch-healing efficiency was measured at 95% after five cuts.
In summary, we described a homogenous and electrically conductive graphite/bPEI composite dough with a conductivity of 1.98 S cm⁻¹. The composite dough exhibited a shear-thinning viscoelastic behavior, different from the predominantly viscous behavior of bPEI alone. The viscoelastic conducting composite dough had unique capabilities, including repetitive rapid self-healing at ambient temperature (with a 10 s recovery duration, 59% of mechanical healing efficiency and 98% of electrically conductive healing efficiency), piezoresistivity, being mouldable into bulk parts or films, and good adhesion to stretchable substrates. These properties enabled a straightforward fabrication of conductors on elastomer substrates by stencil printing. The conductor printed on TPU was highly stretchable (conductance loss of less than 25% at 50% strain) with desirable characteristics, such as stable conductive restoration during repeated stretching cycles and touch-healing of disconnected circuits. These materials could be of interest in the biomedical, robotic, energy and biomimetic fields.

Acknowledgements

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 656467.

Notes and references

A graphite composite dough exhibited rapid mechanical and electrical self-healing properties at ambient conditions and had potentials for highly stretchable conductor applications.