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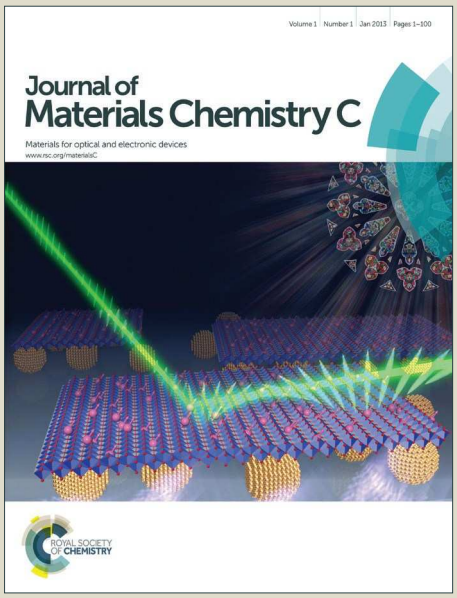

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COMMUNICATION

A mechanically and electrically self-healing graphite composite dough for stencil-printable stretchable conductors

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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,[1] 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.[2-5] 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.[6] 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.[7]

Inspired by the self-healing ability of the skins from mankind and animals, self-healing conductors are receiving growing attention,[7-15] especially in a number of advanced electronic fields, such as supercapacitors,[16-18] lithium-ion batteries,[19] thermal sensors,[20] chemical sensors,[21] and electronic skin.[22, 23] Self-healing chemistry is of great technological interest,[19, 24-28] because the self-healing feature is expected to not only enhance the product lifetime and durability, but also open new opportunities in many fields.[23] 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.[29] Another is the combination of supramolecular elastomers with conducting fillers.[22, 23] 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.[30, 31] The self-healing elastomer can act multiple times, providing repeatable recovery of mechanical and electrical properties. Lately, Oh andcoworkers[6] 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.[32-34] 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.

Branched polyethylenimine (bPEI) is a room-temperature liquid polymer which is rich of various amine groups (i.e. primary, secondary and tertiary amines).[21] As shown in Fig. 1a, bPEI exhibits a well-defined predominantly viscous behavior (the loss modulus (G") dominating the storage modulus (G'), G" > G') in the range of frequencies analyzed.[35] 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.[36] 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

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value for the self-healing polyborosiloxane composite based on reduced graphene oxide scaffold (0.9 S cm^{-1}).[23] 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.[37] 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[38] 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 wettability 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.[6]

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.[10] 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.[22, 30, 39] 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.[22, 23]

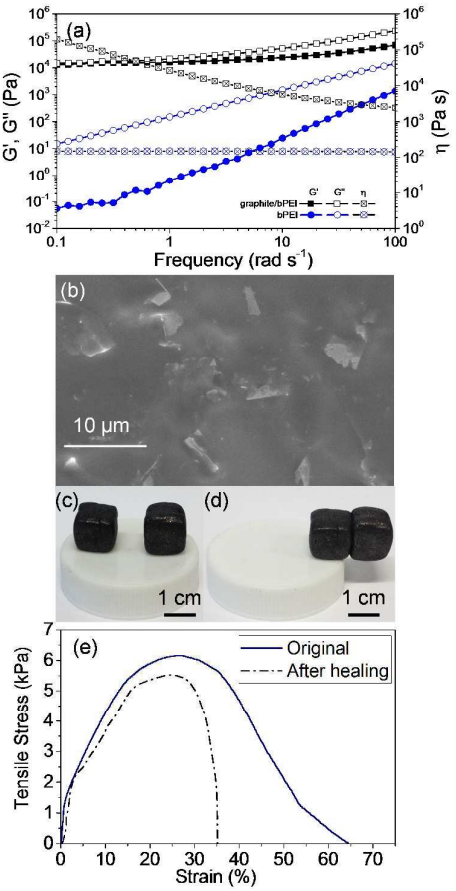

Fig. 1. Mechanical behaviors of graphite/bPEI composite dough. a) Rheological properties of bPEI and graphite/bPEI composite dough. b) SEM image of graphite/bPEI composite dough. (c,d) Demonstration of the self-adhering ability of graphite/bPEI composite dough through gently pressing the two fractured halves together. (e) Typical tensile stress-strain curves of original and healed samples at room temperature. To heal the sample, the two fractured halves were pressed together by applying a gentle pressure of ~1 kPa for 2 s, and then allowed to stand still for over 8 s for further healing.

Fig. 2a describes the time evolution of a typical electrical healing process: an open circuit was formed following complete fracture of graphite/bPEI; once the two fractured halves were brought into contact, the conductivity increased and the resistance dropped to dozens of ohms in 2 s. After a total recovery duration of 10 s, the conductivity returned to close to its initial value. The conductive healing efficiency η_{elec} is defined as the proportion of conductivity restored relative to the original conductivity. A 10 s recovery duration resulted in a nearly full restoration of the electrical properties, with a value as high as 98%. It is noted that electrical healing is more efficient than mechanically healing, which is in agreement with the observation on other self-healing composites.[22] This is because that the mechanically healing process depends on the molecular mobility of polymer segments, which is relatively slow. Fig. 2b shows repeatable restoration of electrical performance in graphite/bPEI under successive cuts at the same location with

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high η_{elec} (97% after five cuts). A circuit was constructed to demonstrate further the potential of self-healing for electronic circuits, as shown in Fig. 2c. Graphite/bPEI also exhibits a piezoresistive response, offering the potential to mimic the pressure sensing capability of human skin. Fig. 2d shows the variation of resistance with applied pressure, measured using an enclosed parallel-plate structure with our self-healing graphite/bPEI sandwiched between two metal conductors (Fig. 2d Inset). The increase in conductivity is exponentially dependent on stress, which enhances the proximity of conducting particles (i.e. graphite). With our experimental setup, we have observed a linear relationship between the logarithm of the resistance ($\log_{10}$ R) and the applied pressure from 30 up to 500 kPa, which is close to the medium pressure range that can be recognized by human skin (10 – 100 kPa).[1] Fig. 2e shows the dynamic resistance variation of graphite/bPEI with the repeated application of 400 kPa pressure, revealing good reproducible dynamic responses.

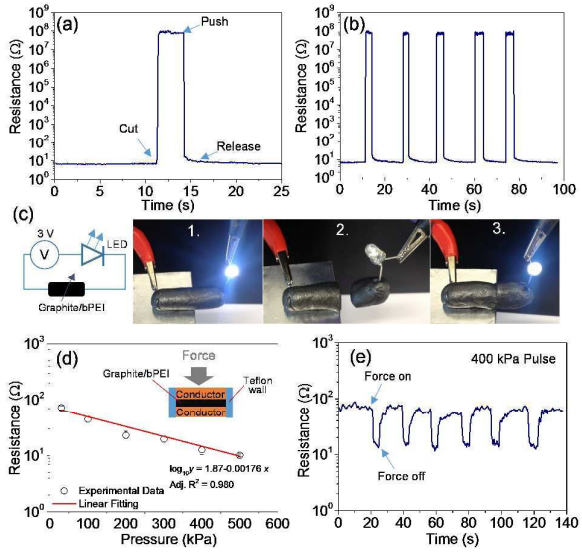

Fig. 2. Electrically self-healing and piezoresistive characterization of graphite/bPEI composite dough. a) Time evolution of the electrical healing process using resistance measurements at room temperature. To heal the samples, the two fractured halves were pushed together by applying a gentle pressure of ~1 kPa for 2 s and then allowed to recover for another 8 s. b) Repeated electrical healing for five cuts at the same severed location. c) Circuit schematic with an LED in series with a self-healing electrical conductor and demonstration of the healing process: 1. undamaged graphite/bPEI (LED on); 2. completely severed graphite/bPEI (open circuit, LED off); 3. electrical healing of graphite/bPEI (LED on). d) Piezoresistive response of graphite/bPEI to increasing pressure values (inset: sensor schematic). Equation represents fitting relationship of resistance and applied pressure. e) Repeated piezoresistive behavior of graphite/bPEI, showing a well-defined and highly reproducible response.

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 raise afterward. This basically matches the stretching and contraction strains of up to 55% generated by the movements of human joints.[40, 41] 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 circles. 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.[6] This rapid, stable touch-healing was highly reproducible shown in Fig. 4b. The conductive touch-healing efficiency was measured at 95% after five cuts.

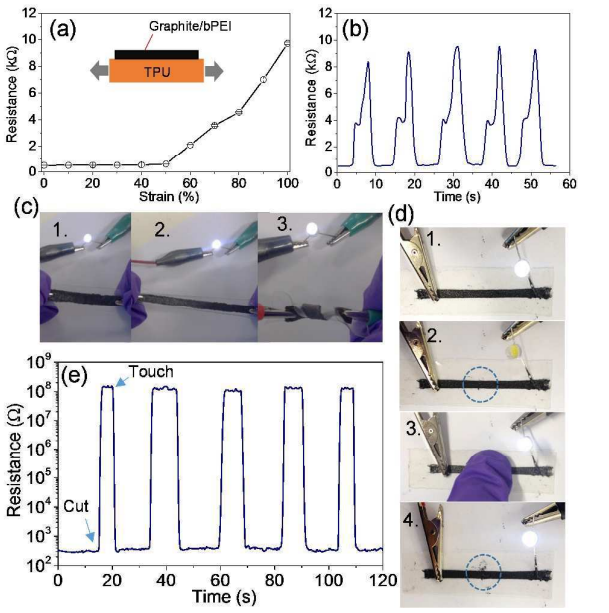

Fig. 3. Electrical properties of graphite/bPEI composite sheet placed on a TPU rubber. a) Resistance of graphite/bPEI as a function of the strain (inset: setup schematic). b) Time evolution of resistance during repeated stretching cycles (100 % strain), showing a well-defined and highly reproducible self-healing. c) Demonstration of a deformable graphite/bPEI/TPU conductor: 1. original; 2. under 50 % strain; 3. twisted. d) Demonstration of touch-healing graphite/bPEI/TPU conductor: 1. original; 2. cut at the dash cycle; 3. electrically touch-healing with a finger touch for 2 s; 4. healed. e) Repeated electrical touch-healing for five cuts at the same severed location.

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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.

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