Graphene–Polyurethane Coatings for Deformable Conductors and Electromagnetic Interference Shielding

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Electrically conductive, polymeric materials that maintain their conductivity even when under significant mechanical deformation are needed for actuator electrodes, conformable electromagnetic shielding, stretchable tactile sensors, and flexible energy storage. The challenge for these materials is that the percolated, electrically conductive networks tend to separate even at low strains, leading to significant piezoresistance. Herein, deformable conductors are fabricated by spray-coating a nitrile substrate with a graphene–elastomer solution. The electrical resistance of the coatings shows a decrease after thousands of bending cycles and a slight increase after repeated folding-unfolding events. The deformable conductors double their electrical resistance at 12% strain and are washable without changing their electrical properties. The conductivity–strain behavior is modeled by considering the nanofiller separation upon deformation. To boost the conductivity at higher strains, the production process is adapted by stretching the nitrile substrate before spraying, after which it is released. This adaption meant that the electrical resistance doubles at 25% strain. The electrical resistance is found sufficiently low to give a 1.9 dB $\mu$ shielding in the 8–12 GHz electromagnetic band. The physical and electrical properties, including the electromagnetic screening, of the flexible conductors, are found to deteriorate upon cycling but can be recovered through reheating the coating.

1. Introduction

Electronics are ubiquitous in everyday life with the next generation of devices aiming to be fully flexible, conformable, wearable, and stretchable.[1–6] Indeed, the flexible electronics market is forecasted to increase annually by 11% and reach a market size major of 40 billion dollars by 2024.[7] One of the most established fields of stretchable electronics is strain sensing,[3] which can be used in the motile parts of robots and machines,[4,8] record the movement and physiological signals in the human body[9–12] and measure mechanical deformation of solid structures.[13–18] The predominant figure of merit for strain sensors is a high gauge factor, i.e., the highest linear change in the electrical resistance as a function of deformation.[19,20] However, numerous applications (e.g., stretchable interconnects, wearable displays, capacitive tactile sensors, printed circuit boards, deformable supercapacitors) demand stretchable conductors that maintain their electrical conductivity upon deformation and thus require a very low gauge factor, ideally zero.[21–28]

Stretchable conductors are commonly achieved by combining elastomeric matrices with conductive materials to form percolated composites. Typically the reinforcing fillers are metallic (e.g., silver nanowires/nanoflakes or copper nanowires) [29,30] or carbon-based.[22,23,31–33] Polydimethylsiloxane (PDMS) is predominantly used as the matrix in research but nitriles, natural rubbers, and polyurethanes are also common.[2,9,21,34–36] Alternatively, the application of conductive materials (e.g., graphene) on a pure elastomer substrate is employed.[24,25,32,37] Recently, the combination of these two techniques, i.e., the application of a stretchable conductive nanocomposite coating on an elastomer, has been proposed for stretchable electrodes.[21,33] Amongst the conductive carbon-based materials, graphene nanoplatelets (GNPs) and multiwalled carbon nanotubes are available in the industrial scale at a moderate price and usually are effective at lower weight concentration levels compared to the metallic nanoparticles. Carbon nanotube-based deformable electrodes have shown promising results,[22,23,31,32,38,39] whereas graphene-related materials have been thoroughly investigated for strain sensing applications,[14,40–42] their use as stretchable conductors is rare.[22]

Several approaches have been used to minimize the decrease in conductivity of flexible conductors upon deformation. One option is a conductive coating applied on a substrate which is then patterned, encapsulated, and/or applied to prestretched materials.[32,35,43] Alternatively, nanofillers can be used to form
a percolated network within a bulk composite.[19,22,44] Thus, it is proposed that the application of a thin, stretchable conductive nanocomposite on an elastomer could exploit both these strategies to give improved performance. Another challenge for deformable conductors is the permanent damage induced by deformation[2,34] and thus the ability to heal such damage is highly desirable. A fundamental area of electronics that would benefit from the manufacturing of deformable and healable conductors is electromagnetic interference (EMI) shielding[44–53] given that EMI shielding is typically achieved with rigid metals.[47]

Herein, we have produced electrodes with sheet resistances of $\approx 10 \ \Omega \cdot \text{sq}^{-1}$ by spray-coating a nitrile rubber substrate with elastomeric, conductive solutions. The sprayed solutions comprised GNPs and a thermoplastic polyurethane (TPU) binder. The final conductor thus consisted of a layered structure with a thin stretchable conductive nanocomposite on the elastomer substrate. The resistance of the GNP–TPU conductors was found to slightly change after repeated bending and folding cycles. The electrodes were washable without any detectable change in their electrical properties and doubled their initial electrical resistance at 12% elongation. A simple semiempirical model of the dependence of the electrical resistance on strain is proposed and discussed also. Repeated stretch–release cycles produced a mechanical deterioration of the electrical properties that can be restored through a simple heating treatment. This healing procedure restored the electromagnetic interference shielding efficiency also. Finally, prestretching the rubber substrate before spraying the conductive ink enhanced the electrical resistive stability of the electrodes.

2. Results and Discussion

2.1. Spray-Coating and Film Morphology

Nitrile substrates were spray-coated with solutions of TPU containing GNPs. This methodology was chosen due to its innate scalability. GNPs (Avanzare AV240) were used with chloroform as the solvent. The GNPs were a conductive reinforcement grade and possessed a large flake diameter and highly graphitic nature. The lateral size of the GNPs was $17 \pm 12 \ \mu \text{m}$ and their Raman spectrum showed a strong 2D peak and a D/G ratio of 0.38 (see Figures S1 and S2, Supporting Information).

After spraying, the samples were heated to 170 °C for 20 s to remove the chloroform and soften the TPU to give a nanocomposite coating that conformed to the underlying nitrile substrate (Figure 1A). The polymers used are thermally stable up to 200 °C and the softening point of the TPU was 150 °C.[21,54] Loadings of 1 to 40 wt% GNPs were used relative to the mass of the TPU in final coating. The 40 wt% coatings were difficult to produce due to the high particulate content blocking the spray gun and thus were used for the initial concentration dependency studies only.

Scanning electron microscopy showed that the uncoated nitrile rubber had a wrinkled surface with macroscale roughness (Figure 1B), which should improve the mechanical lock-in of the coatings applied to it.[55] The heat-treated GNP–TPU films formed a uniform coating on top of the nitrile substrate with a well-adhered interface between the coating and the nitrile (Figure 1C,E; Figure S3, Supporting Information). The nitrile substrate thickness was $\approx 100 \ \mu \text{m}$ (Figure 1D) and the final coatings were $\leq 10 \ \mu \text{m}$ in thickness, with the thickness being dependent on the concentration of GNPs used (Figure 1E; Figure S4 and Table S1, Supporting Information).

2.2. Electrical Characterization of the Graphene-Based Coatings

The sheet resistance of the GNP–TPU was $10^{10} \ \Omega \cdot \text{sq}^{-1}$ at low GNP loading, dropped to $10^{6}–10^{5} \ \Omega \cdot \text{sq}^{-1}$ between 4 and 6 wt% loading and reached $9 \ \Omega \cdot \text{sq}^{-1}$ at the highest loading of 40 wt% GNPs (Figure 2A). This behavior was modeled using classical percolation theory

$$\sigma = \sigma_0 \left( \Phi - \Phi_c \right)^t$$

(1)

where $\sigma$ is the electrical conductivity that can be calculated using the thickness of the conductive layers on top of the nitrile (Table S1, Supporting Information), $\sigma_0$ is the electrical conductivity of the nanofiller employed, $\Phi$ is the filler loading, $\Phi_c$ is the percolation threshold, and $t$ is the universal critical exponent.[56,57] Fitting to the experimental data found $\Phi_c$ as 3 wt% and $t$ as 2.9. This value of the exponent, $t$, might be expected if the GNPs formed a 3D network, however, since their diameters are greater than the film thickness, layered structures are more likely. We speculate that the high value for $t$ is maybe due to significant interflake electron hopping in the direction perpendicular to the surface.

The key performance characteristic of flexible connectors is a minimal change in their electrical resistance upon deformation, i.e., as low a gauge factor as possible. This deformation may be either in axial tension or bending mode. The electrical resistance of the samples was recorded as function of applied tensile strain, $\varepsilon$ (Figure 2B). A 30 wt% loading of GNP was used in the coating (denoted “GNP–TPU” from now on) since it gave the lowest electrical resistance. Moreover, lower loading showed a higher piezoresistivity (Figure S5, Supporting Information). Each sample was stretched up to 100% strain at 4% strain intervals. The current (I) flowing through the samples under a constant voltage of 1 V was recorded at each step (Figure 2B). The current was found to decrease with a power law behavior, with the electrical resistance doubling at 12% strain. At 40% elongation the conductive elastomer preserved $\approx 10\%$ of the initial current flow and above 80% elongation $< 0.5 \ \mu \text{A}$ current flowed through the samples. One reason for this increase in the electrical resistance with strain was the loss of contact between the GNP flakes inside the polymer matrix.[58] Second, the SEM images of the stretched coating revealed many large-scale cracks that formed on the surface of the coatings already at 30% strain (Figure 2B; Figure S6, Supporting Information). It should be noted that a number of applications, such as electrodes for actuators, would use strains significantly less than this 30% strain. Upon release from 100% strain, the deformable electrodes recovered the $(25 \pm 8)\%$ of their initial conductivity. Repeated cycles at 100% strain did not alter the recovered current upon release of the strain without further cracking occurring.
For applications, it is important to predict the dependence of the electrical resistance on $\varepsilon$. Development of a model from first principles based on the polymer physics of the composite coating is nontrivial since it would need to consider the Poisson’s ratio, the interface of the GNPs and TPU, changing orientation of the GNPs, etc. Accordingly, such a model is beyond the scope of this paper. Instead, we have taken a semiempirical approach where the separation of particles due to strain was assumed to reduce the effective volume concentration of the GNPs by a factor $(1 + \varepsilon)^2$. Thus, on increasing $\varepsilon$, the effective volume fraction of GNPs reduces such that the system tends toward the lower concentration of the percolation curve, increasing sheet resistance (see Figure S7, Supporting Information). The model is more fully elaborated in the Supporting Information and results in the relative change in conductivity at a strain $\varepsilon$ being given by

$$\frac{I}{I_0} = \left(1 - \frac{(\varepsilon - 2)\varepsilon}{(1 - \varepsilon)^2 (\Phi - \Phi_0)}\right)^t \quad (2)$$

Least-squares fitting of Equation (2) to experimental data yields $\Phi_0 = 2.9\% \pm 0.8\%$ and $t = 2.9 ± 0.1$ with coefficient of determination, $r^2 = 0.99$; this is shown by the solid line passing through the data in Figure 2B; we note the agreement of our estimates of $\Phi_0$ and $t$ obtained here with those arising from our percolation experiments, as shown in Figure 2A.

Flexible conductors may be used also in bending mode, for example, in polymer actuator electrode applications. Thus, the coatings were subjected to bending tests, where the electrical resistance ($R$) was measured in a flat configuration ($R_{\text{flat}}$) and when the material was curved with a 0.4 cm bending radius ($R_{\text{bending}}$). The initial flat resistance, $R_0$, of the sample was 12 $\Omega$ sq$^{-1}$. The relative change in resistance when in flat and bent morphologies, $R_{\text{flat}}/R_0$ and $R_{\text{bending}}/R_0$, upon subsequent bending cycles is shown in Figure 2C. It was found that both $R_{\text{flat}}$ and $R_{\text{bending}}$ followed the same trend: they increase for the first few cycles but then decreased upon further bending such that after $\approx$50 cycles they returned to their initial values. This declining trend in $R/R_0$ was continued to the end of the test, leading to a decrease of the electrical resistance after 30 000 bending cycles of 4% and 5% for the $R_{\text{flat}}$ and $R_{\text{bending}}$, respectively. The enhancement of the electrical properties after repeated mechanical deformations due to self-organization/recombination of the nanofiller inside the TPU matrix has also been reported in the literature for a polyurethane–gold$^{[59]}$ and polyurethane–GNP$^{[54]}$ nanocomposite systems. Considering practical applications, it is significant that our conductive elastomer can be subjected to tens of thousands of bending cycles without any pronounced increase of electrical resistance.

Flexible conductor was subjected to extreme bending such that would be found in a foldable device or clothing; the conductor was folded in half (i.e., 180$^\circ$) and unfolded repeatedly (Figure 2D)$^{[60]}$. To ensure a consistent fold, the fold edge was compressed with a 1.5 kg weight on each cycle. The ratio $R_{\text{flat}}/R_0$ transverse to the fold line direction for 20 fold–unfold cycles is shown in Figure 2D. After the first cycle, the resistance...
increased by roughly 30%. At the 10th fold– unfold event, $R/R_0$ reached a plateau with an increase of around the 40% of $R_0$ which is then maintained until the 20th folding cycle. SEM revealed micrometric cracks in the coating the region of the creased created by the folding cycles which explains this change in the resistance (see Figure S8, Supporting Information). Nevertheless, the percolating network of the nanofillers was preserved, demonstrating a remarkably low sheet resistance of 17 $\Omega$ sq$^{-1}$ after 20 folding cycles.

The mechanical properties of the nitrile rubber, pure TPU-coated nitrile (TPU-nitrile), and GNP–TPU materials were studied (Figure 2E; Figure S9, Table S2, Supporting Information). The Young’s modulus measured up to 10% strain ($E_{10}$) of the pure nitrile was 5.7 ± 0.2 MPa. The substrate coated with a pure TPU films displayed identical mechanical behavior within error. The GNP–TPU coating, however, made a significant difference to the mechanical behavior despite the coating being ≈10% of the thickness of the underlying nitrile substrate. The

Table 1. Comparison of EMI shielding performances of different materials (rGO = reduced graphene oxide).

| 2D material | Substrate and composite details | 2D material loading | Frequency range [GHz] | EMI SE [dB $\mu$m$^{-1}$] | Ref. |
|-------------|---------------------------------|---------------------|------------------------|---------------------------|-----|
| GNP         | Cellulose network               | 20 wt% rel. to cellulose acetate | 500–750 | 0.6 | [71] |
|             | coated with cellulose acetate-GNP ink |                     |                      |                           |     |
| GNP         | Cellulose                       | 30 wt% rel. to zein + aleuretic acid | 500–750 | 0.9 | [70] |
|             | coated with zein, aleuretic acid, and GNP ink |                     |                      |                           |     |
| GNP         | Printer paper                   | 50 wt% rel. paint   | 500–750 | 1.2 | [73] |
|             | coated with acrylic paint and GNP ink |                     |                      |                           |     |
| rGO         | PET                             | 19 vol%             | 8.0–13.0             | 4.8 | [68] |
|             | coated with polyelectrolyte and rGO |                     |                      |                           |     |
| GNP         | Water-borne polyurethane–graphene thin composite | 25 wt% | 8.2–12.4 | 0.4 | [74] |
| rGO         | rGO latex composite             | 25 wt%              | 8.2–12.4             | 0.06 | [75] |
| GNP         | Nitrile rubber                  | 30 wt% rel. to TPU  | 8.0–12.0             | 1.9 | This work |
|             | coated with TPU and GNP         |                     |                      |                           |     |
GNP–TPU coating with 30 wt% GNP introduced an elastic region up to 20% strain with a significantly increased \( E_\text{I0} \) of 16.1 ± 1.6 MPa. This \( E_\text{I0} \) corresponds to approximate modulus of the GNPs of 0.5 GPa, assuming that the coating and substrate could be approximated by the slab model for the rule of mixtures at such low strains and the GNPs were aligned.[61] Interestingly, the modulus commonly used for elastomers, \( E_\text{I0} \), which is taken at 100% strain, is similar for all the samples, as is their mechanical behavior at higher strains. This observation, combined with the macroscale cracking observed by SEM, in the stretching samples, suggests that between 20% and 30% strain the coating start to fail due to tearing and no longer reinforces the underlying substrate. Above 150% strain the GNP–TPU coating follows the stress–strain curve of the bare nitrile due to the failure of the coating.

Finally, a conductor that maintains its original electrical resistance after numerous laundry cycles is of paramount importance for wearable devices.[62,63] Therefore, the elastomeric conductor was laundered in water–detergent solution under stirring at 40 °C for 1 h.[63,64] Before and after each washing cycle the water–detergent solution was replaced in order to guarantee that each cycle was performed with a suitable high surfactant concentration. As can be seen in Figure 2F, the ratio \( R/R_\text{o} \) was constant during 10 washing cycles. The high washing stability of the conductor is a result of the excellent adhesion between TPU and nitrile rubber that was found to be of \( \approx 1 \) N m\(^{-1} \) in a previous report.[20] This result is better compared with textiles functionalized with TPU–GNPs inks.[64]

### 2.3. EMI Shielding of the Deformable Conductors

Flexible and stretchable EMI shielding materials are fundamental for the implementation of conductive and flexible devices.[45–48,65–67] Indeed, a large-scale diffusion of flexible electronics is impossible if an electronics apparatus cannot maintain a negligible interference between its electrical components when deformed.[66,67] For this reason, the EMI shielding effectiveness of the conductive elastomer was tested depending on the amount of nanofillers employed (Figure 3), and before and after repeated stretch–release cycles (Figure 5).

The EMI shielding measurements were conducted at frequencies between 8 and 12 GHz (X-band) on transmittance. These frequencies are used in smartphones, televisions, and microwaves.[68–70] The EMI shielding effectiveness (SE) represents the losses in the incoming electromagnetic wave due to screening and is usually calculated using

\[
\text{SE(dB)} = -10 \log_{10}(T)
\]

where \( T \) is the transmittance and represents the ratio between the transmitted and the incident electromagnetic power and is a function of the frequency of the incoming EM wave.[71] In Figure 3, the transmittance is plotted as a function of the frequency of the incident EM waves. At low nanofiller loadings (minor of 5 wt%), the samples did not display any significant electromagnetic shielding effect (0 dB attenuation, 4 wt% loaded sample plotted as an example). Increasing the filler loading, the SE increased with increasing nanofiller loads such that the 30 wt% GNP–TPU samples exhibited a transmittance of \( \approx -17.2 \) dB. Normalized for thickness (Table S1, Supporting Information), the best GNPs-based sample screened 1.9 dB \( \mu \text{m}^{-1} \). These normalized results are comparable with state-of-the-art attenuation levels (in the order of \( \approx 1 \) dB \( \mu \text{m}^{-1} \)) of other carbon-based nanocomposites.[68,72–75]

### 2.4. Healing Mechanism of the Conductive Elastomers

As discussed earlier, the conformable conductors showed hysteresis in their conductivity when deformed significantly. It was postulated that this damage could be healed through heating and resoftening the TPU, allowing the tears to heal and the percolated network to readjust. This concept was explored by applying a 1 V bias to the conductive GNP–TPU samples and then elongating them to 50% strain. This strain would be appropriate for stretchable electronics applications such as tactile sensors and deformable printed circuit boards.[21] The force on the sample was then released and a heat gun was used to heat and resoften the TPU coating at 170 °C. This deformation and healing process was cycled four times. The initial current \( I_0 \), current at 50% strain \( I_{50} \), current after each release before heat treatment \( I_{\text{RTD}} \) and current after the heat treatment \( I_{\text{Heat}} \) were measured (Figure 4A). \( I_{50} \) was <10% of \( I_0 \) for the samples and upon release \( I_{\text{RTD}} \) conductivity returned to 30–40% of \( I_0 \), showing that permanent damage had occurred. As anticipated, the heat treatment restored the conductivity of the samples \( I_{\text{Heat}} \) in the figure of the samples to values above \( I_0 \). Examination in the SEM confirmed that the heating had healed the cracking within the GNP–TPU samples.

The mechanical properties of the samples at each step of the stretch–release cycles were also tested assuming the crosshead position to measure displacement. The samples were strained to 30% elongation with their stress–strain curves given in Figure 4B. The crosshead was then returned to its initial position at which point the samples buckled slightly due to
the permanent deformation that occurred during the test. The stress–strain curve was then retaken (named GNP–TPU No Heat). In this last test, the stress did not immediately rise at the start of the test due to slack that had occurred from the permanent deformation. The samples were then heated using a heat gun (“Healed” in the figure) and restretched to 50% elongation. The Young’s modulus measured at 10% strain ($E_{10}$) of the GNP–TPU samples was influenced by the healing treatment (Figure S10, Supporting Information). It was found that the heating partially restored the Young’s modulus for the GNP–TPU samples, taking $E/E_0$ from $\approx 0.45$ to $0.70–0.80$ after healing.

Stretch–release cycles also had an influence on the EMI shielding of the conductive elastomer. The transmittance of the conductive elastomer was tested before and after repeated 100% elongation (Figure 5, for 50% elongation see Figure S11, Supporting Information). The initial transmittance for the GNP–TPU sample ($T_0$), its value after 1 stretch–release cycle (GNP–TPU–Cycle 1), and the value after 9 stretch–release cycles (GNP–TPU–Cycle 9) are reported in Figure 5A. The repeated strain reduced the initial shielding effectiveness. The samples preserved $\approx 75\%$ of $T_0$ after the 9th strain cycle (Figure S12, Supporting Information). Considering the thickness (see Table S1, Supporting Information), the GNP–TPU–Cycle 9 sample was able to screen $\approx 1.4$ dB $\mu$m$^{-1}$. Even after repeated stretch–release cycles, the results are comparable with state of the art attenuation levels (of order 1 dB $\mu$m$^{-1}$) of other carbon-based nanocomposites. The stretch-induced reductions of the transmittance were once again healed by a simple heat gun procedure identical to the fabrication process (Figure 5B).

The increase in the transmittance with the heat gun treatment agrees with the similar increase seen in conductivity.

2.5. Prestretching of the Rubber to Improve the Stretching Stability

The prestretching of elastomeric substrates before the application of a conductive layer can enhance the stability of the electrical performance of the obtained material. Thus, the nitrile rubber was biaxially stretched by 50% and then spray-coated.

Figure 4. A) The measurements of the current under repeated stretch–release cycles at 50% stretch for the GNP–TPU samples with 30 wt% GNP. $i_{STO}$ is the current in the samples with the stretch back to zero. After each stretch–release cycle a heating process performed with a simple heat gun permits to heal the performance loss. B) The stress–strain curves till 50% elongation of the 30 wt% sample at different conditions: after fabrication (GNP–TPU), after 50% elongation without the heating treatment (GNP–TPU No Heat) and of the GNP–TPU samples after heating (GNP–TPU Healed).

Figure 5. A) Transmittance of the GNP–TPU sample before and after repeated stretch–release cycles at 100% elongation. The transmittance after 1 stretch–release cycle (GNP–TPU–Cycle 1) and the value after 9 cycles (GNP–TPU–Cycle 9) are reported. B) Healing of the transmittance with a simple heat gun procedure analogous to the fabrication process for the GNP–TPU samples.
The biaxial strain was then released and the coating heat treated to anneal it (Figure 6A). The coating formulation studied contained 30 wt% of GNP (PRE–GNP–TPU). An optical microscope image of the final conductor showed that the coating was very compliant (see Figure S13, Supporting Information).

The prestretch production process was found not to affect the initial resistance of the samples but did significantly improve the conductivity under deformation (Figure 6B). In the first part of the current–stretch curve, the PRE–GNP–TPU samples exhibited the best performance. At 12 % elongation the PRE–GNP–TPU samples preserved 80% of their initial current flow at a constant voltage. The gauge factor of the PRE–GNP–TPU sample was only 2 compared to 7 for the original GNP–TPU samples. The resistance of PRE–GNP–TPU doubled at 25 % strain. This performance is better than a bulk polyurethane–GNP composite[54] and a chemical vapor deposited graphene layer on PDMS, [76] which showed an order of magnitude increase in the electrical resistance at 25% stretch. Li et al.[77] with a hybrid GNP–molybdenum disulphide coating on PDMS.

Our model for the strain dependence of conductivity was extended to account for prestreain by assuming linear dependence for applied strains below the prestrain and that Equation (2) extended to account for prestraining by assuming linear dependence on PDMS.

4. Experimental Section

Materials: GNPs were obtained from Avanzare (grade AVA240) and were fully characterized (lateral size and Raman spectrum of the nanoflakes are presented in Figures S1 and S2, Supporting Information, respectively). TPU was purchased from BASF (Elastollan 1185A12) and was used as polymer matrix. Nitrile rubber (acrylonitrile butadiene) was obtained from Kimberly-Clark. Typically, the conductive polymeric solution contained 0.2 g of dry TPU and a certain percentage of GNPs, indicated throughout the text as wt% ratio relative to the amount of polymer. For example, a conductive elastomer containing 30 wt% GNPs translates into a polymeric slurry having 0.06 g of GNPs. The solvent employed was chloroform (16 mL for every 0.2 g of dry TPU) acquired from Sigma-Aldrich. The conductive solution was sonicated (750 W, 20 kHz, 40% amplitude, six times for 30 s, Model Num. VCX750) to achieve an adequate dispersion. After that, 4.5 mL of dispersion was spray-coated (2.0 bar, 15–18 cm distance) on the rubber substrate (7.5 × 5) cm². A heat gun was employed (~170 °C, 20–25 cm distance, 30 s) to ensure the complete evaporation of the solvent and to enhance the adhesion. The temperature was measured using a thermocouple. For the fabrication of the prestretched samples, the rubber substrate was biaxially stretched of the 50% with orthogonal clamps before the application of the coating. The clamp distance was controllable simply using a screw. The sample preparation procedure was then identical to the one described above.

Methods: SEM pictures of the topography and of the cross-section of the samples were acquired with a Zeiss Evo50 microscope (acceleration voltage of 10 kV). For cross-sectional SEM images, the specimens were frozen in liquid nitrogen and fractured.

The electrical percolation threshold was determined using a source-meter from Keithley (model 2450) in four-probe configuration. Silver conductive paint (RS pro, product number 186–3600) was painted creating 5 mm wide contacts on the samples (7.5 × 5) cm² spaced by 5 mm.
The degradation due to repeated bending cycles was determined using a custom built assembly. During bending cycles, samples (2 × 1) cm² were suspended between two supports. One of the supports was fixed in place while the other could oscillate horizontally along a rail system.

A pneumatically controlled (Festo Model ADN-20-50-A-P-A) cylinder with an electronically switched solenoid valve (Festo Model VUVG Metric MS 5/2) was used to induce the oscillation of the moving support. To quantify the degradation, surface resistance readings were normalized to a baseline value, determined prior to any bending cycles. Four small contacts were applied to the edge of each sample using silver conductive paint (R5 pro, product number 186-3600). The baseline and all subsequent surface resistance values were obtained by sweeping a DC current (Keithley Model 6221) between two contacts and measuring the resultant voltage across the other two contacts (Keithley Models 2182A). Each time, current flowed in parallel to the direction that the oscillating sample support moved. The bending cycles were periodically paused to allow normalized surface resistance readings with the sample in a flat (released) or curved orientation (bent).

The folding stability of the electrical properties after repeated stress cycles was measured recording the resistance variation transverse to the fold mark. The source-meter coupled with a uniaxial testing machine (Instron 3365). The dimensions of the specimens was (2 × 1) cm².

Washing cycles were completed by washing the conductive elastomers in water (volume of ~500 mL, dimension of the sample (7.5 × 5) cm²). Ten washing cycles of 1 h were performed. During the cycles, a water movement was maintained employing a magnetic stirrer and keeping the temperature of the water constant at 40 °C. After each cycle, a detergent (Cussons Carex Complete, ~4 mL) was added.[34] The sheet resistance was measured with the setup described above before and after each cycle.

The J–V curves of various samples for determination of the electrical properties changes under stretching and after healing by annealing, were measured in two probe configuration. The effect of stepwise and repeated deformation on the current of the nanocomposites was characterized by the source-meter coupled with a uniaxial testing machine (Instron 3365). The samples were clamped on the testing machine and electrodes were connected to the specimen’s ends. The samples were cut in a dog bone shape with a distance between the silver contacts of 25 mm. Current was recorded applying a constant potential of 1 V with and without stretch. During stepwise tests, the elongation was increased by 4% at each step with a rate of 10 mm min⁻¹. At each single step, deformation was held for 20 s to permit the sample stabilization, and afterward the current was measured. For the cyclic tests, each cycle was performed with an elongation of the 50% of the initial length (strain rate of 10 mm min⁻¹), then released back to zero strain. At the end of each cycle, a heat gun procedure identical to the manufacturing process was performed to heal the material. At each stage of the cycle, the current flowing in the specimens was recorded. The uniaxial testing machine (Instron 3365, 500 mm min⁻¹) was also utilized for measuring the stress–strain characteristics of the stretchable conductors.

The EMI shielding effectiveness of the specimens was recorded using a vector network analyzer (Keysight N5227A) and two WR-90 (8.2–12.4 GHz) waveguides. The transmittance was recorded between 8 and 12 GHz. The dimension of the samples was (3 × 4) cm². Raman spectra of the GNPs were obtained using a Renishaw inVia Raman spectrometer using an excitation wavelength of 514 nm.

Optical microscopy images were taken using a VHX digital microscope from Keyence. The measurements described in this section were performed on at least three different samples.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

conformable electronics, healable electronics, piezoresistivity, stretchable electronics, thermoplastic polyurethane

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