Supramolecular Gels

Facile Supramolecular Processing of Carbon Nanotubes and Polymers for Electromechanical Sensors

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Dedicated to Dr. Junkyoung Kim on the occasion of his 60th birthday and to KIST-Jeonbuk on the occasion its 10th anniversary

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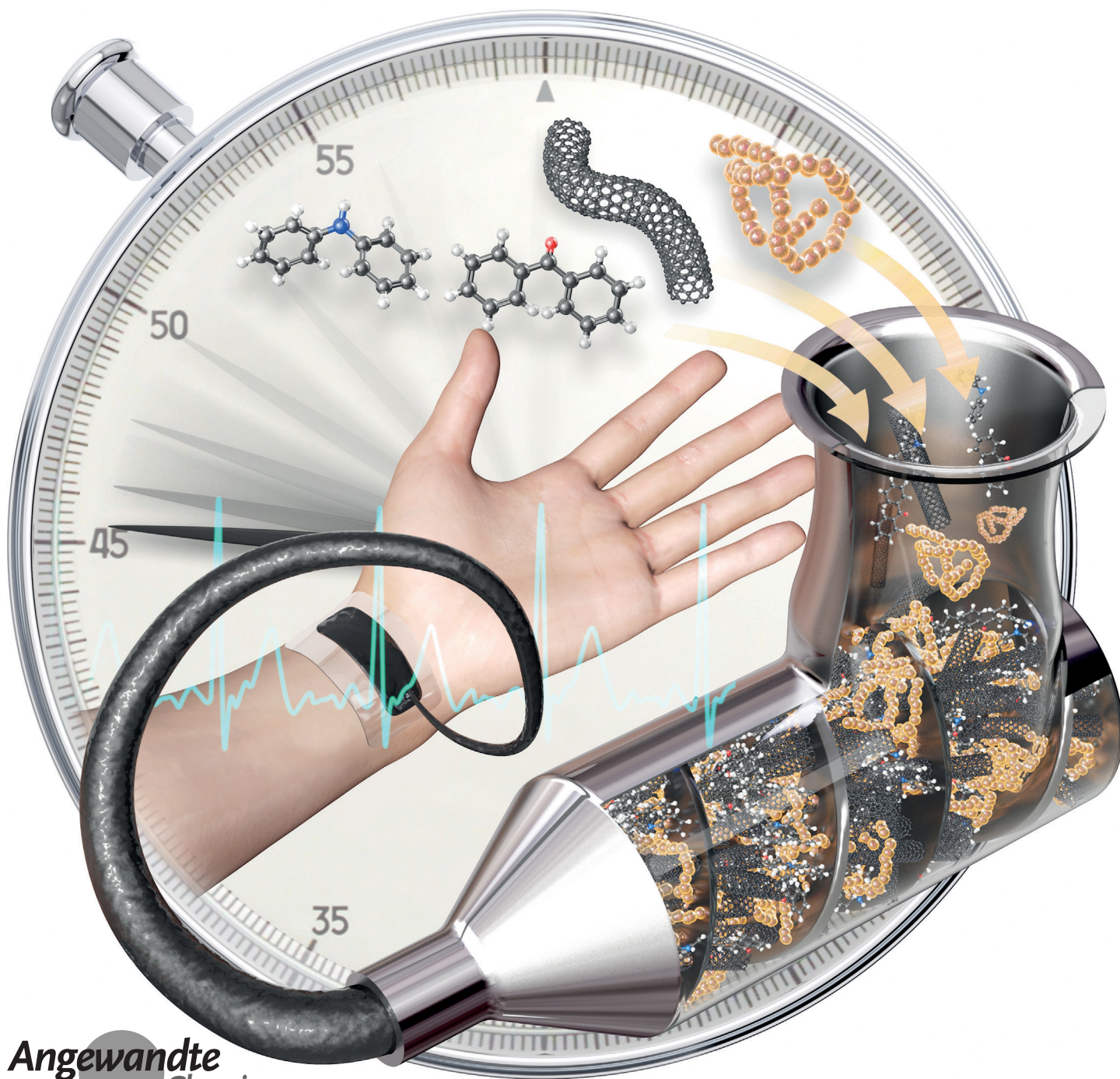
Abstract: *We herein report a facile, cost-competitive, and scalable method for producing viscoelastic conductors via one-pot melt-blending using polymers and supramolecular gels composed of carbon nanotubes (CNTs), diphenylamine (DP), and benzophenone (BP). When mixed, a non-volatile eutectic liquid (EL) produced by simply blending DP with BP (1:1 molar ratio) enabled not only the gelation of CNTs (EL-CNTs) but also the dissolution of a number of commodity polymers. To make use of these advantages, viscoelastic conductors were produced via one-pot melt-blending the EL and CNTs with a model thermoplastic elastomer, poly(styrene-b-butadiene-b-styrene) (SBS, styrene 30 wt%). The resulting composites displayed an excellent electromechanical sensory along with re-mendable properties. This simple method using cost-competitive EL components is expected to provide an alternative to the use of expensive ionic liquids as well as to facilitate the fabrication of novel composites for various purposes.*

Supramolecular interactions play key roles in improving the properties of composite materials via interfacial phenomena between the multiple materials. For numerous approaches used to fabricate functional composite materials, the supramolecular dispersion and/or gelation of carbon nanomaterials is a key pre-step for achieving many applications[1–5] including electronics,[6–9] electrocatalysts,[10,11] and electromechanical sensors.[12] Some elegant dispersants based on oligo(*p*-phenylenevinylene)s have also achieved lyotropic bucky gels with carbon nanotubes (CNTs), showing interesting photophysical and surface characteristics.[13] Ogoshi and Harada et al. showed unique sol-gel transitions of CNTs dispersions triggered by molecular host–guest interactions, which laid a fundamental basis for self-healing conductors.[14] In addition, various studies have reported that some liquids can give bucky gels of CNTs once mixed.[15] Among many liquids to disperse CNTs, ionic liquids (ILs) have been considered as a strong candidate due to their long-term stability derived from negligible volatility[16–18] along with a unique ability to make a bucky gel of CNTs via simple grinding.[17]

Bucky gels, as we and others have revealed, are advantageous for generating highly conductive elastomers and electrocatalysts via additional processes.[6–8,11] However, making polymer–carbon composites using dispersed carbon nanomaterials still requires tedious processes, and it is difficult to impart viscoelastic and re-mendable characteristics. These characteristics are particularly important to realizing highly sensitive and healable electromechanical sensors.[12,19] To produce such polymer–carbon composites, a recent study described a use of viscoelastic composites with dispersed graphene (graphene in silly putty) as a highly sensitive electromechanical sensor that can measure various mechanical events.[12] However, the preparation of the sensor using graphene–polymer composites requires long and tedious steps including dispersion of graphene using toxic and volatile organic solvent followed by the solvent removal.

Herein, inspired by eutectic welding in metallurgy, we explored the use of a non-volatile organic eutectic mixture for the realization of viscoelastic polymer–carbon composites with re-mendable characteristics. We found that a supramolecular eutectic liquid (EL), consisting of diphenylamine (DP) and benzophenone (BP),[20] can not only dissolve a number of commodity polymers but also form bucky gels (EL-CNTs) with single-walled CNTs (SWCNTs) upon grinding. To our knowledge, this is the first study to report the use of EL as a gelator for CNTs. Thus, a viscoelastic conductor composed of EL, CNTs, and polymers could be efficiently prepared via one-pot melt-blending, which the approach is cost-effective, and easily scalable. The resulting viscoelastic conductor exhibited excellent electromechanical sensory and also possessed re-mendable characteristics.

DP can be melted by physical contact with BP, whose carbonyl moiety is a hydrogen acceptor for DP (Figure 1a,b). Also, their opposite electrostatic potentials induce attraction between the two components (Figure 1a).[20] The electrostatic potential was calculated using density functional theory (DFT) methods and the calculation details are described in Supporting Information. Upon mixing, the solids of DP and BP became yellowish liquid owing to the charge-transfer interaction, and a 1:1 molar mixture of DP and BP remained in a liquid state at 25°C (Figure 1b, Figure S1 in the Supporting Information). We recognized interesting features of the supramolecular EL consisting of DP (m.p. = 50–53°C, surface tension: $\gamma = 39.3$ mJ m^{-2} at 60°C) and BP (m.p. = 47–51°C, $\gamma = 45.1$ mJ m^{-2} at 20°C), which are compatible with not only CNTs but also with various polymers. Based on Coleman's approximate expression, the supramolecular EL ($\gamma_{EL} = 33.76$ mJ m^{-2} at 20°C) seems compatible with CNT surfaces owing to the van der Waals and π–π interactions.[3] For estimating surface tension of EL, EL contact angle on a polymeric surface with a known surface energy was measured and the values were fitted to Young's equation (Figure S2).

Grinding the EL with SWCNTs (TUBALL™, diameter < 1–2 nm, length > 5 μm) gave a viscous bucky gel (EL-CNTs) within a few minutes (Figure 1b). All the SWCNTs

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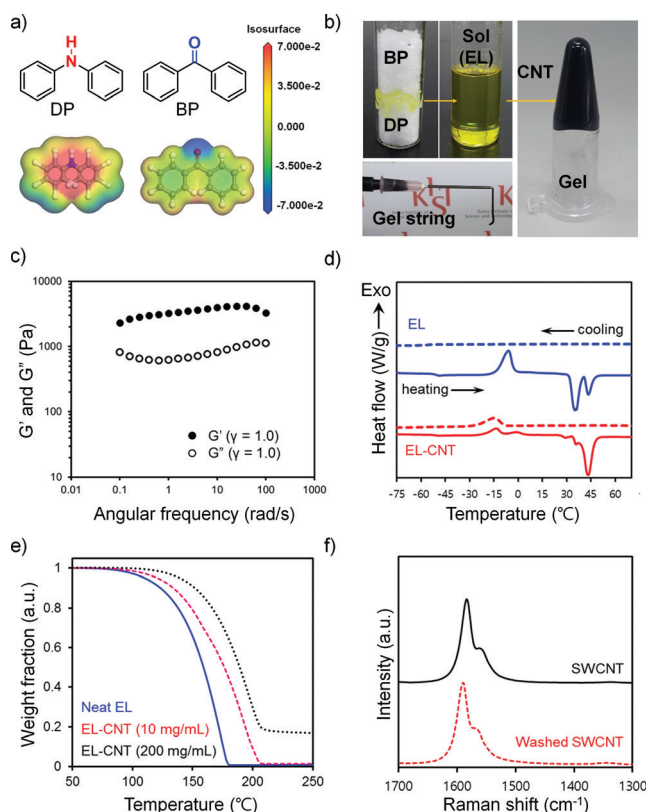https://doi.org/10.1002/anie.201708111.

Figure 1. Supramolecular gelation of single-walled carbon nanotubes (SWCNTs) with diphenylamine (DP) and benzophenone (BP). a) Chemical structures and electrostatic potentials of DP and BP. b) A solution of EL and a supramolecular gel of EL containing SWCNTs (EL-CNTs, 10 mg CNTm⁻ EL). c) Angular frequency dependencies of dynamic storage (G′) and loss modulus (G″) of EL-CNTs (10 mg CNTm⁻ EL) at 25°C (applied strain amplitude, γ = 1.0). d) Differential scanning calorimetry (DSC) thermograms of EL alone and EL-CNTs (10 mg CNTm⁻ EL). e) Thermogravimetric analysis (TGA) of neat EL and two different concentrations of EL-CNTs gel (10 mg CNTm⁻ EL and 200 mg CNTm⁻ EL). f) Raman spectra of the purified SWCNT and the SWCNT obtained from the EL-CNTs (10 mg CNTm⁻ EL) by washing with methanol.

were used after removal of metallic impurities prior to formation of the gel or other composites. The resulting EL-CNTs could be extruded through a syringe needle to form a continuous string (Figure 1b). A rheological study of EL-CNTs revealed the existence of an elastic network structure, implying the incorporated CNTs were de-bundled. As shown in Figure 1c, at an applied strain of 1, the dynamic storage modulus (G′) curve of EL-CNTs showed a plateau region in the frequency dispersion curve, showing gel like characteristics where the storage modulus (G′) was greater than the loss modulus (G″) and the G″ revealed no signature of relaxation.

Differential scanning calorimetry (DSC) revealed that EL-CNTs was essentially different from EL alone (Figure 1d). Upon heating, neat EL showed a glass transition at −50.5°C, an exothermic peak at −7.5°C, and two endothermic peaks at 35°C and 43°C, possibly corresponding to fusion of BP-DP co-crystal.[20] In sharp contrast, upon heating, EL-CNTs exhibited a glass transition at −50.3°C along with two

exothermic peaks at −14.5°C and −1.1°C and multiple endothermic peaks predominantly at 44.0°C, whereas upon cooling, it showed an exothermic peak at −14.4°C. The presence of endothermic peaks at higher temperature for EL-CNTs than EL implies that EL molecules near the CNTs surfaces melted at higher temperatures owing to their synergistic interaction. To further investigate the interaction between EL and CNTs surface, thermogravimetric analysis (TGA) was performed using neat EL and EL-CNTs at two different concentrations (Figure 1e). As the amount of CNTs increased, the decomposition temperature of the sample increased, confirming the presence of favorable interaction between EL and CNTs. Raman spectroscopy showed the CNTs were identical upon gelation without any chemical denaturation (Figure 1f).

We also found that a series of polymers, including poly(styrene-*b*-butadiene-*b*-styrene) (SBS, $M_W = 140$ kDa, styrene 30 wt%), poly(ethylene-*co*-vinyl acetate) (EVA, melt flow index = 57 g/10 min, vinyl acetate 40 wt%), poly-(methyl methacrylate) (PMMA, $M_W = 120$ kDa), and poly-styrene (PS, $M_W = 192$ kDa), can be solubilized in EL upon heating (Figure 2b). In contrast, the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulphonyl)imide (BMITFSI, m.p. = −4°C, γ = 33.6 mJ m⁻² at 20°C), which
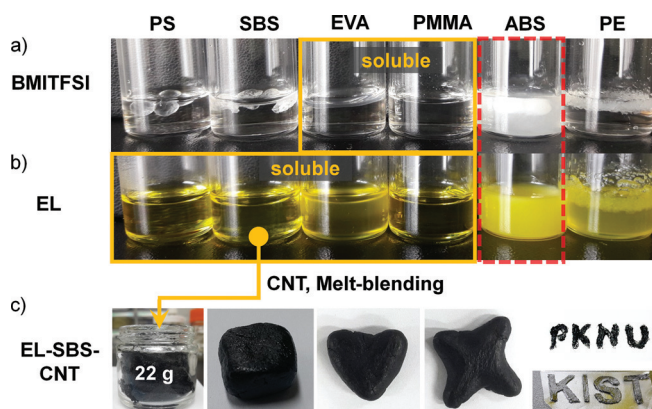

Figure 2. a) Solubility tests of a series of polymers (0.1 g mL⁻¹) in BMITFSI and b) in EL. c) Photographs of moldable, viscoelastic, and printable EL-SBS-CNTs composites.

has a surface tension similar to that of EL,[21] could not solubilize non-polar polymers such as SBS and PS (Figure 2a). Poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS, melt flow index = 25 g/10 min) was partially soluble and polyethylene (PE, $M_W = 35$ kDa) was insoluble in both BMITFSI and EL. Coupled with a fact that the surface tension of EL is close to surface energy of many organic polymers, we believe a presence of π–π interactions along with van der Waals force would help EL to dissolve polymers with aromaticity such as PS and SBS, while hydrogen bonds and van der Waals forces would help EL to solubilize polymers possessing carbonyl groups, such as EVA and PMMA.

The compatibility of EL with various polymers as well as with CNTs (see Figure 1e) suggests EL-CNTs can be easily

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melt-blended with polymers soluble in EL using less shear force than the one needed without EL. In particular, melt-blending of CNTs with EL-EVA or EL-SBS at 150 °C produced viscoelastic composites, EL-EVA-CNTs and EL-SBS-CNTs, respectively. For all EL-polymer-CNTs composites, a ratio of EL and polymer was fixed at 1:2 in weight while the amount of CNTs was varied. In typical plots of storage (G') and loss (G'') moduli versus oscillatory strain amplitude, γ_0, both G' and G'' drastically decreased upon mixing with EL as compared to neat SBS and EVA (Figures S3 and S4). This indicates EL acted as a plasticizer for the matrix polymers. It is noteworthy that compositing CNTs with SBS at 150 °C was failed without addition of EL owing to a high viscosity of neat SBS at 150 °C.

Interestingly, among the EL-polymer-CNTs composites, we found that EL-SBS-CNTs displayed easily moldable and re-mendable characteristics. Similar to somewhat stiff "silly putty" with viscoelasticity, various shapes of EL-SBS-CNTs dough could be formed (Figure 2 c). In addition, EL-SBS-CNTs was printable on a polymeric surface via pressing, demonstrating a potential usage in multiple areas including wearable electronics.[22] Although one-pot melt-blending of BMITFSI, EVA, and CNTs was performed, the resulting composite (BMITFSI-EVA-CNTs) severely coagulated during the blending. In addition, BMITFSI was easily squeezed out from BMITFSI-EVA-CNTs (Figure S5). On the other hand, EL-EVA-CNTs and EL-SBS-CNTs were well mixed during the blending, and EL was securely trapped in the matrices (Figure S5). Exploiting EL for compositing CNTs with polymers, therefore, is practically beneficial since less shear force is needed and no tedious processes such as use of toxic, volatile solvents and/or solvent recovery steps are required.

Both the electrical conductivity and mechanical properties of EL-SBS-CNT composites increased with increasing CNTs content (Figure 3 a,b). Compared to a non-conducting EL-SBS sample, addition of 6.1 wt % CNTs yielded EL-SBS-CNTs composite possessing conductivity of 0.14 S m$^-$. Also, both shear G' and G'' increased as CNTs content increased. The G' at strain amplitude 0.001 % increased by 24 % by adding 6.1 wt % of CNT compared to the EL-SBS composite,

reaching a level similar to those reported in the literature.[12] Owing to a negligible volatility of EL at ambient conditions, the viscoelastic natures of EL-SBS and EL-SBS-CNTs were maintained.

To further study viscoelasticity of the resulting EL-SBS-CNTs composite, time evolution of CNT networks was monitored via electrical resistance of the composite after applying a tensile step-strain (2 %). A schematic describing the experimental setup for this measurement is shown as Figure 4 a. Detailed experimental description can be found in the Supporting Information. The resistance sharply increased once the step strain was applied at $t = t_0$, which the resistance subsequently decayed in a power law (Figure 4 b). As observed and illustrated in the literature,[12,23] this behavior is interpreted as the following: a rapidly applied deformation first broke the CNT networks within the EL-SBS-CNTs composite, which the networks then reformed over time via
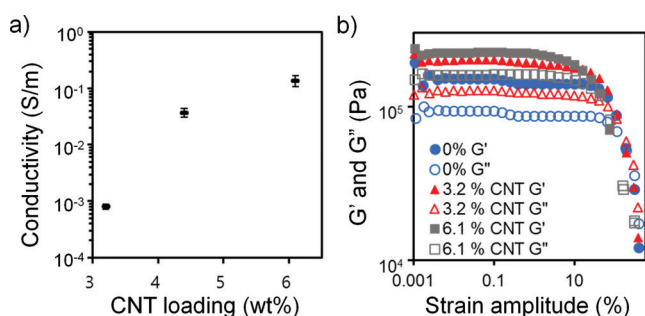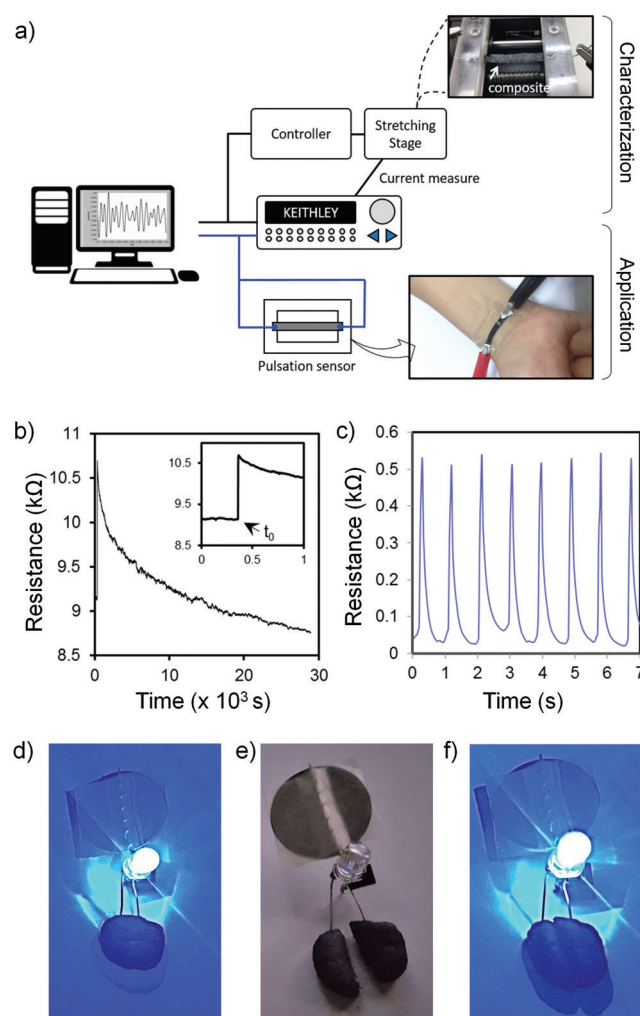

Figure 3. a) Conductivity as a function of CNT loading. Error bars are standard deviation calculated from five measurements on the identically prepared samples. b) Storage (G') and loss (G'') moduli of EL-SBS-CNTs composites as a function of shear strain amplitude at various CNT loadings. Angular frequency was 6.28 rad s$^-$ for this measurement.

Figure 4. a) Characterization and application system of EL-SBS-CNTs composites. b) Time evolution of electrical resistance of EL-SBS-CNTs composite (6.1 wt % CNTs) exposed to a 2% tensile step strain at $t = t_0$. Inset: expansion of the early time region. c) Electrical response measured using EL-SBS-CNT composite (6.1 wt % CNTs) to sense pulse. Photographs of light obtained from an LED lamp circuit connected by d) the EL-SBS-CNTs composite, e) after damaging the composite, and f) after healing the composite with gentle pressure.

induced dipoles under the applied field as well as diffusion of CNTs. This confirms the viscoelasticity of our composites possessing high motilities of the polymer chains and CNTs. This was because the EL molecules act as a plasticizer in the SBS matrix, which the fact was also evidenced by the aforementioned shear moduli drops of the polymer matrix upon addition of EL (Figure S3 and S4).

As a practical application using our EL-SBS-CNTs composite, blood pulsation sensing test was conducted. A thin, pressed conformal composite film with thickness approximately 100 μm was placed onto the human wrist without any adhesion layer (Figure 4a). The composite film was fixed to a plastic supporting holder so that the EL-SBS-CNTs based device can be tightly attached to the wrist while sensing the pulsation. As Figure 4c shows, the EL-SBS-CNTs composite on the wrist detected electrical resistance changes arising from blood-vessel deformation thus effectively acted as a pressure sensor. Additionally, since viscoelastic materials can easily be molded and retain their original shapes by applying pressure, we also demonstrated that our composites can be healed after damaging the composite. As shown in Figure 4d, an LED lamp circuit connected by the conducting EL-SBS-CNTs lit. However, once the composite was disconnected by damage, the lamp turned off (Figure 4e), which the lamp lit again after healing the composite by applying gentle pressure (Figure 4f).

A one-pot melt-blending of elastic polymers and a supramolecular gel composed of EL and CNTs resulted in the facile preparation of a viscoelastic composite possessing unprecedented electromechanical properties as well as re-mendable characteristics. These conductive, healable composites displayed high electromechanical sensitivity to mechanical stimulus, and thus they may find applications in a range of fields.

Conflict of interest

The authors declare no conflict of interest.

Keywords: carbon nanotubes · electromechanical sensors · eutectic liquid · supramolecular gel · viscoelastic conductor

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