Highly Stretchable, Self-Healable Elastomers from Hydrogen-Bonded Interpolymer Complex (HIPC) and Their Use as Sensitive, Stable Electric Skin

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Supporting Information

ABSTRACT: There is a growing interest in developing stretchable strain sensors to quantify the large mechanical deformation and strain associated with the activities for a wide range of species. Herein, we constructed elastomeric, healable hydrogen-bonded interpolymer complex (HIPC) rubberlike film by complexation of hydrogen-bond (H-bond)-donating poly(acrylic acid) (PAA) and H-bond-accepting poly(ethylene oxide) (PEO) (or poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (F108)). All HIPC elastomers prepared from varied PAA/PEO (or PAA/F108) ratios are healable elastomers with high extensibility (with the highest strain of 1400%). Recovery of all films can automatically occur or be accelerated by externally added water droplet. The stress- and strain healing efficiencies ($\eta_s$ and $\eta_\epsilon$) of the water-assisting healed PAA/F108 blends are as high as 99%. Furthermore, stretchable and healable conductor films were fabricated from silver nanowire-printed (Ag-p) and the single-walled carbon nanotube-blended (SW-b) conductor films, respectively. The healable Ag-p conductor film is an ultrasensitive strain sensor, exhibiting large electric resistance variation when stretched. In contrast, the healable SW-b film is an ultrastable strain sensor with reversible resistance strain response over 200 stretching release cycles within a high strain range of 500%. Therefore, this study provides a new and flexible HIPC strategy for the fabrication of stretchable, ultrasensitive, and stable self-healing electrode materials.

INTRODUCTION

Stretchable, wearable, flexible, and human-friendly soft electronic devices have boosted the development of various smart devices, such as sensors, light-emitting diodes (LEDs), lithium-ion batteries, and supercapacitors. Stretchable electrodes with high toughness play a crucial role in integrating various devices together to support functions under large mechanical deformations. During the past few years, several representative strain sensors using carbon nanotube (CNT), metal/semiconductor, graphene, and conductive polymer as conductive components combining with elastomeric substrates have been successfully fabricated. Among them, silver nanowires (AgNWs) were frequently used as conductor for flexible electronics, particularly for high-performance strain sensors with great electrical and mechanical properties. In general, AgNWs were deposited on large-area flexible and stretchable substrates using solution-coating techniques such as printing, spin coating, dip coating, etc. However, the AgNW-deposited electrodes generally lack self-healing ability due to the poor adhesion between AgNWs and substrates. Moreover, CNT were often applied in the strain sensor as conductor, in which the main sensing mechanism is the change in resistance at the CNT/CNT junctions when the network is stretched. In general, CNTs were deposited on flexible substrate as a separate layer, resulting in electrodes that can only be subjected to small perturbation (a strain below 5%). Failure of the electrodes is also attributed to the poor interfacial adhesion between CNT and substrate. Overall, the AgNW- and CNT-deposited electrodes have several limitations with regard to the substrates, such as poor interfacial adhesion, limitation of elongation, and lack of self-healing ability. Therefore, it is of interest to address these limitations in stretchable conductors. Especially for stretchable and self-healable composite electrodes usually prepared by mixing a stretchable self-healing polymer matrix and a conductive material, fabricating skin-inspired elastomer conductors that are stretchable and self-healable with good interfacial adhesion and with matched modulus between electrode and human tissue is highly challenging.

Self-healing materials have attracted increasing attention recently. In general, the automatic self-healing process may involve an irreversible or a reversible mechanism. The irreversible system has the common inherent drawback that it can heal only once. Therefore, more recent research works have been concentrated on reversible system that can repeatedly break and heal upon external stimuli. Reversible system can be based on either covalent interaction, such as Diels–Alder and...
retro-Diels–Alder,25,26 or noncovalent interactions, such as H-bonding,27–29 ionic bonding,30 metal coordination,31 or π–π stacking.32 Because of its flexible and dynamic nature, H-bond is one of the most well-known physical interaction forces applied for the preparation of reversible self-healing materials. Several previous examples illustrated the use of H-bond interactions in constructing self-healing materials. Poly(vinyl alcohol)33 (PVA) hydrogel, from the freezing/thawing method, can self-heal at room temperature without any stimulus (e.g., heating). However, the soft PVA hydrogel can only be stretched to 400% before fracture. A facile one-step approach was used to construct self-healing antifogging films based on partly cross-linked PVA and poly(acrylic acid) (PAA). Abundant free hydroxyl groups in the cross-linked films contribute to the antifogging property.34 However, the inferior mechanical properties of the cross-linked films limited their use as stretchable electric components. To sum up, hydrogels showed smart intrinsic self-healing characteristics toward wounds caused by external forces, which is attributed to sufficient free groups at the scratched interfaces to reform H-bonds across the interfaces and a sufficient chain mobility that is indispensable for chain diffusion across the interfaces and association to reform H-bonds. Therefore, we attempted to use two polymers with the respective H-bond-donating and -accepting groups to generate hydrogen-bonded interpolymer complex (HIPC)35 elastomers, which was traditionally used in the solution state as drug carriers,36,37 with self-healing property. The stretchable, self-healable HIPC elastomers can be further used as the flexible substrate of an electric sensor.

Herein, we reported the design and preparation of a series of HIPC elastomers, wherein PAA was mixed with different amounts of poly(ethylene oxide) (PEO) or F108 (Scheme 1) to prepare stretchable and healable elastomers as flexible substrate for the AgNW and single-walled carbon nanotube (SWCNT) conductors. The constituent and composition of the respective PAA/PEO and PAA/F108 systems determine the mechanical and healing properties of the elastomers, which will be primarily discussed. On the basis of the high extensibility (1400%) and superior healing property (both ηηε and ηε reach 99%), PAA/F108 1/9 was chosen as the flexible component to prepare the respective AgNW-printed (Ag-p) and SWCNT-blended (SW-b) electric sensors for study. In the presence of hard AgNWs (or SWCNT) component, the Ag-p (or SW-b) sensor is nevertheless a self-healable elastomer capable of detecting bending and stretching motions and exhibits a high stretchability (>1000%). Moreover, the Ag-p and SW-b conductor films were constructed in different configurations, that is, AgNWs of Ag-p film are deposited as a layer separate from the polymer substrate, whereas SWCNTs of SW-b film are homogenously mixed with the polymer substrate. Configurations of the conductor films thus determined their role as a stable and reliable strain sensor. Recovery of the conductivity of the strained Ag-p after being released to the relaxed state can only be attained within small strain (<50%) range. In contrast, recovery of the electrical property of the relaxed SW-b sensor can be achieved even after large stretching deformation (500%). Overall, the present methodology developed paves the way for practical applications of highly stretchable self-healing strain electronic devices.

**RESULTS AND DISCUSSION**

**Qualitative Evaluation of the Self-Healing HIPC Blends.** PAA/PEO x/y and PAA/F108 x/y (x/y refers to the molar ratio between H-bond-donating carboxylic acid and H-bond-accepting oxygen atom of ethylene oxide unit) blends
were prepared and their self-healing behavior can qualitatively be evaluated from the three experiments illustrated in Scheme 2.

First, rubberlike films of PAA/PEO 1/9 and PAA/F108 1/9 were cut by a knife (top left) and the cut marks of the rejoined PAA/PEO 1/9 and PAA/F108 1/9 films became invisible at 90 and 60 min after the cuts, respectively. The inherent soft poly(propylene oxide) (PPO) block of F108 is responsible for the superior healing efficiency of PAA/F108 1/9, which will be discussed later.

Second, the externally added water droplet was found to accelerate the healing process. As illustrated in Scheme 2 (top right), the wounds covered by water droplet completely healed after the vaporization of the water droplet in few seconds. In this case, the water molecules act to mobilize the hydrophilic PEO and PAA chains in the fracture interphase to close vicinities to have intimate H-bond interactions, therefore healing the fracture interphase with accelerated rate. A similar experimental result was found in H-bonded films derived from complexation of PEO and tannic acid. Instead of adding water droplets, the fractured PEO/tannic acid sample was exposed to humid environment to accelerate the healing.

The HIPC blends are all with high healing efficiency, which can be primarily evaluated from the third experiments (bottom). The fractured elastomeric films were cut, rejoined, and left untouched for 30 min to generate healed specimen for test. The results suggest that the healed interphases should be very strong because they can sustain an extension for at least 10 and 14 times the initial lengths of the PAA/PEO 1/9 and PAA/F108 1/9 films (Movies S1 and S2), respectively. Besides the healing efficiency, PAA/F108 1/9 is also a better elastomer with higher fracture strain compared to PAA/PEO 1/9.

Fourier Transform Infrared (FTIR) Analysis. As illustrated in Scheme 1, the possible H-bond interactions in the elastomer complexes can be classified into two modes, self-association between two carboxylic acids of PAA and interassociation between carboxylic acid of PAA and oxygen atoms of PEO (or F108). In this respect, FTIR analysis (Figure 1) is a powerful tool for analyzing the possible H-bond interactions involved in the blends. As reported previously, conversion of self-associated carboxylic acids into inter-associated carboxylic acids gradually shifted the carbonyl stretching band to longer wavenumber. Therefore, the increase of PEO (or F108) content in the blends shifts the carbonyl stretching band of PEO/PAA (or PEO/F108) from 1718 to 1730 cm$^{-1}$ (or 1732 cm$^{-1}$). The carbonyl stretching band in the corresponding spectral region can be deconvoluted into self- and interassociated bands. The result (Table S1) coincides with the trend that fraction of interassociated carbonyl absorption increases with the increase of PEO (or F108) content in the blend. Enhanced interassociated carbonyl absorption refers to the prevalent interpolymer interactions of the HIPC blends.

FTIR analysis also provides information regarding the major morphological change of the blended elastomers. Semicrystalline PEO exhibits two characteristic crystalline peaks at 1343 and 1360 cm$^{-1}$ (Figure 2), respectively. In contrast, no such crystalline peaks are present in the spectra of the blends, which contain only broad band, representative of the amorphous PEO segments in the elastomers, over the corresponding absorption region. In the blends, PEO segments must interassociate with PAA chains intimately, leading to the destruction of the regular crystalline packing (Figure S4). As a matter of fact, all HIPC blends are amorphous according to their transparent appearances (Figure S5) and the differential scanning calorimetry (DSC) results provided below.

Differential Scanning Calorimetry (DSC) Analysis. DSC analysis provides information regarding the amorphous nature of the blends (Figure 3). Before DSC scans, all blended samples needed to be vacuum-dried to remove the absorbed moisture.
No thermal transition can be detected for all blended samples without preliminary drying. As being semicrystalline, PEO and F108 exhibit the characteristic melting transitions at 64 and 60°C, respectively. The crystalline structure of PEO (or F108) in the blends was nevertheless destructed since all blends exhibit only amorphous glass transition ($T_g$) in their DSC thermograms.
As consistent with FTIR analysis, preferable interassociated H-bond interactions between PAA and PEO (or F108) resulted in miscible, amorphous blends with single, detected $T_g$. For pure PAA, its characteristic $T_g$ at 114 °C is no more preserved in the HIPC blends. The preferable interassociation in the blends results in the gradual shift of the $T_g$ to lower temperature when the PEO (or F108) content in the blends increase. Maximum loads of PEO and F108 in PAA/PEO 1/9 and PAA/F108 1/9 result in the large shifts of $T_g$s to 51 and 42 °C, respectively. The resolved $T_g$s of PAA/F108 x/y are all lower than those of PAA/PEO x/y with the same x/y ratio, which suggests that PAA/F108 blends are softer elastomers with higher chain mobility compared to PAA/PEO blends.

The HIPC blends discussed in this study belong to a class of "physical cross-linked network", within which the interassociated H-bonded PEO segments act as the junction points and the rest of the mobile PEO segments are the bridge units. The increase of PEO content in the blends increase the fraction of mobile bridge units, which leads to the lowering of the detected $T_g$ value. For PAA/F108 system, the PPO segments of F108 are immune from the restriction of H-bonding and are more mobile units compared to the PEO segments. Thus, incorporation of PPO chains in PAA/F108 results in soft blends with lower $T_g$ compared to PAA/PEO. Soft chains with high mobility are beneficial for the diffusion of the ruptured segments to near vicinities, redistributing and activating the interassociated H-bonds to heal the cut or fractured interphases. With this prospect, PAA/F108 blends should represent a better healing system compared to PAA/PEO blends, a point that can be verified by the following mechanical analyses.

**Dynamic Mechanical Analysis (DMA).** The mechanical elastic properties of the rubberlike films were primarily analyzed by DMA. The storage modulus ($E'$) of the PAA/PEO and PAA/F108 films was given as a function of frequency (0–5 Hz) in Figure 4a,b, respectively. The results from both systems suggest that we can tune the film property by adjusting the content of the
soft PEO (or F108) chain in the blends. A previous study\textsuperscript{44} indicated that stiffness and strength of triblock copolymers decrease with increase of the soft block content. Similarly, softer blends with higher soft PEO (or F108) content should exhibit lower $E'$. Comparatively, PAA/F108 $x/y$ films all exhibit lower $E'$ than PAA/PEO $x/y$ films of the same $x/y$ ratio; therefore, PAA/F108 represent a softer system compared to PAA/PEO. All of the results are correlated with the DSC analysis. Again, soft chains in the blends favor the segmental diffusion and facilitate the healing of the cut and fracture surface. The mobile PPO chain of F108 makes PAA/F108 a better healing system compared to PAA/PEO, which can be further verified by rheology analysis.

**Rheology Analysis.** In general, rheological measurement provides variation of the time scale involved in the dynamic relaxation process of the polymer network. Rheology analysis of the present systems should help evaluate the healing process of the cross-linked HIPC blends. The resultant elastic ($G'$) and viscous ($G''$) moduli of PAA/PEO and PAA/F108, at frequency ranging from 0.05 to 126 rad s$^{-1}$, are given in Figure 5a,b, respectively. The moduli $G'$ and $G''$ of PAA/F108 $x/y (x/y = 1/1$ and 1/9) blends are all lower than those of PAA/PEO blends of the same $x/y$ ratio, which is correlated with the DMA result that PAA/F108 is a softer system compared to PAA/PEO system. Moreover, blends with higher PEO (or F108) content are also softer than blends with lower PEO (or F108) content.

The resolved $G'$ and $G''$ curves of the rubberlike films all follow similar paths. At low frequency, $G''$ is greater than $G'$, which refers to liquidlike character, while at higher frequency, $G'$ exceeds $G''$, which corresponds to gel-like behavior. For all tested films, transformation from a low-frequency liquidlike to a high-frequency gel-like states occurs at the point when $G''$ intersected $G'$ (inset, Figure 5). The moduli of PAA/PEO 1/9 intersected at frequency $\omega_c \sim 8.83$ rad s$^{-1}$, corresponding to a relaxation time of $1/\omega_c \sim 0.113$ s; and PAA/F108 1/9 intersected at a frequency $\omega_c \sim 10.18$ rad s$^{-1}$, corresponding
to a fast relaxation time of $1/\omega_c \sim 0.1$ s. After the intersecting point, both curves flattened at higher frequencies and entered into the rubbery plateau region. Compared to blends with 1/9 ratio, PAA/PEO 1/1 and PAA/F108 1/1 blends all relaxed with longer relaxation times of 0.44 and 0.16 s, respectively. A previous study on a self-healing ionic network system concluded that materials with short relaxation time are better in chain mobility and are therefore superior in healing efficiency than materials with long relaxation time. In accordance with the above results, PAA/F108 blends represent better healing system compared to PAA/PEO blends. HIPC blends with higher PEO

Figure 7. Stress–strain curves of virgin and self-healing films of (a) PAA/PEO 1/9 and (b) PAA/F108 1/9; stress healing efficiencies of (c) PAA/PEO $x/y$ and (d) PAA/F108 $x/y$; and strain healing efficiencies of (e) PAA/PEO $x/y$ and (f) PAA/F108 $x/y$ at various healing times.
(or F108) content are also superior in healing property to blends with lower PEO (or F108) content.

Figure 6 shows the robust recovery behavior of PAA/PEO 1/9 and PAA/F108 films by rheological measurements. The rubberlike films were subjected to oscillatory force with alternatively changing amplitudes. At a low strain of 1%, $G'$ is greater than $G''$, and both moduli do not change over time, which implies that both films remained intact under small strain.

Figure 8. Stress–strain curves of virgin and water-assisting healed films of (a) PAA/PEO 1/9 and (b) PAA/F108 1/9; stress healing efficiencies of virgin and water-assisting healed films of (c) PAA/PEO 1/9 and (d) PAA/F108 1/9; and strain healing efficiencies of virgin and water-assisting healed films of (e) PAA/PEO 1/9 and (f) PAA/F108 1/9 at various healing times.
oscillatory strain. When the applied oscillatory strain is high at 200%, \( G' \) drops rapidly and becomes lower than \( G'' \) due to the breakage of physical network. When the applied strain was returned to 1%, the sample immediately recovered to the initial gel-like state (i.e., \( G' > G'' \)) with the same \( G' \) and \( G'' \) values as the first experimental run. Therefore, the disrupted network films were completely recovered, which confirmed the healing ability of PAA/PEO 1/9 and PAA/F108 1/9. Disruption and recovery of the gel properties under different oscillatory shears can be repeatedly conducted for at least three times without causing any change in the film’s oscillatory property. In contrast, the \( G' \) and \( G'' \) values of PAA/PEO 1/1 and PAA/F108 1/1 deviated from the first experimental runs (Figure S2) under repeated oscillatory strain. Films with higher PEO (or F108) content are therefore better in recovery property than films with lower PEO (or F108) content.

**Tensile Test.** To further evaluate the self-healing ability of the blend films, tensile tests were performed in both the virgin (uncut) and healed PAA/PEO 1/9 (Figure 7a) and PAA/F108 1/9 (Figure 7b) films, respectively. The virgin PAA/PEO 1/9 and PAA/F108 1/9 films are all good elastomers with a fracture strain (\( \varepsilon_f \)) of 1100% at a fracture stress (\( \sigma_f \)) of \( \sim 0.45 \) MPa and with \( \varepsilon_f \) of 1400% at a \( \sigma_f \) of \( \sim 0.15 \) MPa, respectively. To the best of our knowledge, \( \varepsilon_f \) (1400%) of PAA/F108 1/9 is the highest strain value reported so far for the self-healing polymeric materials.\textsuperscript{46–48} Benefiting from the reversible H-bond interactions, the healed PAA/PEO 1/9 and PAA/F108 1/9 films are also good elastomers with a common feature that both \( \sigma_f \) and \( \varepsilon_f \) values increased with healing time. If the automatic healing process was allowed to proceed for a long period, i.e., 24 h, the healed PAA/PEO 1/9 and PAA/F108 1/9 actually approached the initial, virgin states according to the resolved values of \( \varepsilon_f = 1000\% \) and \( \sigma_f = 0.39 \) MPa for the healed PAA/PEO 1/9, and \( \varepsilon_f = 1309\% \) and \( \sigma_f = 0.15 \) MPa for the healed PAA/F108 1/9.

Performances of the healed films can be easily evaluated from the healing efficiencies \( \eta_\varepsilon \) and \( \eta_\sigma \) of the healed PAA/PEO \( x/y \) (Figure 7c,d) and PAA/F108 \( x/y \) (Figure 7e,f), respectively. In general, a long healing time is beneficial for the healing efficiencies and films with higher PEO (or F108) content have higher healing efficiencies compared to films with lower PEO (or F108) content. Moreover, PAA/F108 \( x/y \) is superior in healing efficiency, with the resolved \( \eta_\varepsilon \) and \( \eta_\sigma \) values higher than those of PAA/PEO \( x/y \). The calculated \( \eta_\varepsilon \) and \( \eta_\sigma \) are 86 and 90% for PAA/PEO 1/9, and 95 and 94% for PAA/F108, respectively. All of these results are correlated with the comment that softer (or more flexible) chains are beneficial for segmental diffusion of the H-bonding groups and therefore facilitate the recovery of the healed films.

It is also interesting to examine the effect of water droplet regarding the accelerated water-assisting healing process illustrated in Scheme 2. Primarily, water droplet was dripped on the cut surfaces of the sample film and the surfaces were rejoined and left untouched for different times before the tensile analysis. Representative stress–strain curves from the water-assisting healed films of PAA/PEO 1/9 (Figure 8a) and PAA/F108 1/9 (Figure 8b) illustrate the beneficial role of healing time for the tensile property of healed films. The calculated healing efficiencies from the water-assisting healing process were...
compared to those from automatic healing in Figure 8. It is then clear that water droplets are beneficial for the recovery of the damaged films. Healing of the blends were accelerated by water droplet according to the resolved \( \eta_s \) and \( \eta_v \): 88 and 98% for PAA/PEO 1/9, and 99 and 99% for PAA/F108, respectively.

**Conductivity Films.** With the superior mechanical properties, PAA/F108 1/9 was selected as the base material to construct the healable and stretchable conductor sensor. Primarily, AgNWs was used as the conductor to build up Ag-p sensor film. Scanning electron microscopy (SEM) image of the as-printed AgNWs (Figure 9a) was found to be randomly stacked and distributed on the surface of PAA/F108 1/9 film, forming a network structure whose junctions led to the conductivity of the film. Here, besides elongated nanowires in straight geometry, we also observed some curly AgNWs in the network structure. The adhesion between the deposited AgNWs layer and the rubberlike film should be enough to sustain the bending motion (Figure 9b) for more than 100 times without any visual delamination of the deposited AgNWs layer. The flexible Ag-p conductor film was also applied as a self-healing conductor in a circuit (Figure 9c)\(^{49,50}\). The flexible conductor film is conductive enough to transmit electricity in a circuit to an LED. The LED immediately went off after the conductor film was cut into two pieces. However, by bringing the two separated pieces into contact, the conductor film was recovered to result in the light-up of LED. Moreover, the conductance of the flexible Ag-p film could be maintained when the sample was bent (Figure 9d). The above result suggests that this flexible Ag-p conductor can be applied as a wearable sensor capable of detecting bending motion.

The Ag-p conductor film was attached onto a glove (Figure 10a) for the detection of finger joint bending. When the finger bent, the resistance gradually increases from \( \sim 30 \) \( \Omega \) to a maximum of \( \sim 70 \) \( \Omega \). The reversible change of the resistance from \( \sim 30 \) to \( \sim 70 \) \( \Omega \), corresponding to the bending or releasing of the finger, is clearly visible over the cycles. The electric resistance ratio \( (R/R_0) \) (Figure 10b) of the Ag-p conductor film is rather constant about 100% over the 100 bending–releasing cycles. Therefore, the Ag-p sensor can be employed for accurate motion detection of finger joints and could be used as electric skin for robots.

The possibility of using Ag-p conductor film as a self-healing strain sensor was then explored. The Ag-p conductor film can be stretched up to \( \sim 800\% \) without visual fracture of the film. Regarding the good conductivity of AgNWs, the initial resistance of the conductor film is low (60–70 \( \Omega \), Figure 10c).
Afterward, the resistance of the film exhibited a sudden jump at a strain of 100% and then increased monotonously to attain a final value of $1.68 \times 10^7$ $\Omega$ at a strain of 800%. For Ag-p, applying a strain beyond 100% caused the failure of resistance recovery. The Ag-p film nevertheless exhibits reliable response to small strain (Figure 10d), that is, a small strain of 50% contributes to little change of the conductive path and therefore, the resistance of the restored film is the same with the initial value. Displacement of AgNWs and decrease of conductive junction points were suggested to be responsible for the failure of AgNW-printed polyurethane at a strain <100%. However, besides these two possible causes present in the AgNWs layer, the failure mode in the interfacial zone should not be overlooked. As the strain increases, certain AgNWs in the interfacial zone would detach from the polymer substrate, resulting in loss of some conductive paths and the increase of resistance. Extra interfacial zone therefore adds potential failure mode to the Ag-p conductor film.

In contrast to the separate AgNWs layer in Ag-p, the SWCNT conductors of SW-b were directly blended with the HIPC elastomers, forming a miscible system with high sustainability to large strain deformation. The SEM image taken from the vacuum-dried SW-b film is shown in Figure 11a, which exhibits the main feature that the polymer-coated SWCNTs were interconnected with each other and were surrounded by the polymer matrix. As the polymer-coated SWCNTs are intimately and homogeneously connected with the elastomeric polymer matrix, the SW-b conductor film is therefore highly stretchable in sustaining high strain. A large strain of 1000% caused a little deviation of the resistance value when the stretched film was relaxed back to the initial length (Figure 11b). With a lower applied strain of 500%, the relaxed SW-b film exhibited the complete recovery of the resistance to the initial value (Figure 11b, inset) before stretch. Therefore, SW-b is a more reliable stain sensor compared to Ag-p. The healable SW-b film is a ultrastable strain sensor as it exhibited a reversible resistance strain response over 200 stretching release cycles within a high strain range of 500%. Moreover, the electric resistance ratio ($R/R_0$) (Figure 11c) of the SW-b conductor film is quite stable under the bending motion, which remains about 100% over the 150 bending release cycles. The $R/R_0$ values of the sensor remain almost constant with minor fluctuations within 10% in the first 200 cycles strain test (Figure 11d) (between 0 and 500% strain). We thereby suggest that the SW-b conductor film is an ultrastable sensor under bending motion and high strain.
The key parameters of several previous strain sensors, including healable and nonhealable sensors, are listed in Table 1 to compare with the results from the present Ag-p and SW-b sensors. In this work, the healable SW-b strain sensor that we fabricated can sustain a large strain (>1000%), which made it suitable for broad applications and exhibits a good balance between high sensitivity and stability. Among the healable sensors, the SWCNT/PVA/borax sensor is a superior strain sensor with a large \( \Delta R/R_0 \) ratio of 1514% in a large strain range of 1000%. However, this superior strain sensor required high sensitivity with a large \( \Delta R/R_0 \) ratio. With the built-in soft PPO block of F108, the Ag-p sensor film shows high sensitivity with a large \( \Delta R/R_0 \) ratio of 1514% at a strain of 800%. Among the healable sensors, the SW-b film is an ultrastable strain sensor, showing a release of 100% in the strain range of 800%.

### CONCLUSIONS

HIPC blends of PAA/PEO x/y and PAA/F108 x/y are all elastomers with self-healing properties. The results suggest that blends with higher x/y (e.g., 1/9) ratio are softer materials with higher stretchability and healing efficiencies than blends with lower x/y ratio. With the built-in soft PPO block of F108, the PAA/F108 x/y blends are also better system with higher stretchability and healing efficiency than PAA/PEO x/y blends. Among all blends, PAA/F108 1/9 exhibits the best results with the resolved \( \eta_1 \) of 1400% at a \( \sigma_1 \) of ~0.15 MPa, and \( \eta_0 \) and \( \eta_1 \) of the healed blend of 95 and 94%, respectively. PAA/F108 1/9 was further incorporated with AgNWs and SWCNT to construct Ag-p and SW-b conductor films, respectively. Although inferior in the large strain stability, the highly conductive Ag-p film is nevertheless ultrastable with a large \( \Delta R/R_0 \) ratio of 100 000% in the strain range of 800%. In contrast, the SW-b film is an ultrastable strain sensor, showing a stable \( R/R_0 \) ratio over 200 stretching release cycles in the strain range of 500%. The low cost of this HIPC strategy makes it a potential commercial route for fabricating flexible, healable conductor sensors.

### EXPERIMENTAL SECTION

#### Materials

The chemical compounds used are PAA (Mw ~ 100 000, 35 wt % in H2O, Sigma-Aldrich), PEO (Mw ~ 14 000, Sigma-Aldrich), Pluronic F108 (Mw ~ 14 600 with 82.5 wt % of PEO, Sigma-Aldrich), poly(vinylpyrrolidone) (PVP, Mw ~ 58 000, Sigma-Aldrich), ethylene glycol (EG, Alfa Aesar), AgNO3 (Sigma-Aldrich), iron(III) chloride (Acros), and SWCNT-2012 (length <2 μm, purity >97%, Golden Innovation Business Co., Ltd.). The glass substrates used in this work was cleaned by sonication in 2-propanol/water (v/v = 1/1) for 20 min and washed with ultrapure water three times before drying in a vacuum oven. AgNWs used in this work were synthesized according to the reported method.

#### Preparation of AgNWs

AgNWs used in this work were synthesized according to the reported method. The typical experiments were described as follows: 20 mL of ethylene glycol (EG) was injected into a 50 mL three-necked flask and preheated for 30 min; silver nitrate (0.33 g) was added within 10 s while 20 mL of EG solution of poly(vinylpyrrolidone) (PVP, Mw, ~ 58 000) (0.88 g) and FeCl3 (0.0027 g) was injected dropwise by a syringe within 5 min, and then the reaction was maintained at 170 °C for 80 min. The as-obtained products were then filtered and washed with methanol several times, and the purified products were preserved in ethanol.

#### Preparation of HIPC Films

A calculated amount of PEO (or F108) in methanol (5 mL) was added dropwise into a stirred solution of a calculated amount of PAA in methanol (5 mL), then adding 33 wt % of SWCNT into the resultant homogeneous solution was then slowly deposited on the AgNW-printed conductive glass substrate. A clean PAA/PEO 1/9 blend film was then pressed on the AgNW-decorated glass substrate before drying in open air for 1 day, rendering transparent rubberlike films for study.

#### Preparation of Ag-p Conductor Film

Typically, 1 mL of ethanol suspension of AgNWs (25 mg mL\(^{-1}\)) was dropped on top of a glass substrate before drying in open air for 1 day to obtain AgNW-decorated glass substrate. A clean PAA/PEO 1/9 (or PAA/F108 1/9) film was then pressed on the AgNW-decorated glass substrate and then peeled off to result in a AgNW-printed conductive film of PAA/PEO 1/9 (or PAA/F108 1/9).

#### Preparation of SW-b Conductor Film

The films were prepared by adding a calculated amount of F108 in methanol (5 mL) dropwise into a stirred solution of a calculated amount of PAA in methanol (5 mL), then adding 33 wt % of SWCNT into the resultant homogeneous solution.
the resultant homogeneous solution, and then allowing the solution to dry in open air for 1 day.

**Characterization.** FTIR spectra were recorded by a Bruker Tensor 27 FTIR spectrophotometer. The complex solution was deposited on a premade KBr pellet, and the whole assembly was dried in a vacuum oven to prepare specimen for analysis. Thermal transition of the complex was determined by a TA-Q20 differential scanning calorimeter with a scan rate of 10°C min⁻¹. The storage modulus (E') of the films was determined from a PerkinElmer Instruments DMA 8000 apparatus. Sample films with dimensions of 25 mm × 10 mm × 2 mm were used for analysis. Rheology data were obtained by a TA Instruments ARES G2 rheometer equipped with a 2.5 mm parallel plate. Samples with 2 mm diameter were used. Angular frequency from 0.05 to 126 rad s⁻¹ was collected at a strain amplitude of 0.05%, which was within the linear viscoelastic response region. The recovery property was investigated by strain films under an alternatively changing amplitude of oscillatory force at 1 Hz. Tensile test was conducted by a PRO TEST PT-1699 V tensile tester with an extension speed of 30 mm min⁻¹. Films with dimensions of 15 mm × 5 mm × 2 mm were used for analysis. The stress healing efficiency (ησ) was calculated by the formula
\[
\eta_{\sigma} = \frac{\sigma_{\text{v}}}{\sigma_{\text{f}}},
\]
where σ_{\text{v}} and σ_{\text{f}} are the fracture stresses of the virgin and self-healed samples, respectively. The strain healing efficiency (ηε) was calculated by the formula
\[
\eta_{\varepsilon} = \frac{\varepsilon_{\text{f}}}{\varepsilon_{\text{f,h}}},
\]
where \(\varepsilon_{\text{f}}\) and \(\varepsilon_{\text{f,h}}\) are the fracture strain of the virgin and self-healed samples, respectively. SEM images were obtained by a JEOL JSM-6700F microscope operated at 10 kV. The resistance was measured on a Tonghui TH2829 LCR meter. Wide-angle X-ray diffraction (WXRD) spectra were obtained from a Siemens D5000 diffractometer. UV–vis absorption spectra were recorded on an Ocean Optics DT 1000 CE 376 spectrophotometer.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01456.

Table showing deconvolution of carbonyl groups of PAA/PEO 1/9 and F108, and PAA and PAA/F108 1/9; UV-Vis spectra and transparent films of PAA/PEO 1/9 and PAA/F108 1/9 blends; resistance variation of the SW-bent conductor film over different bending times; resistance change of detection of minimal movement by finger touches of Ag-p and SW-b conductor films; self-healing image of SW-b and Ag-p conductor film; electric resistance ratio of the healable Ag-p and SW-b conductor films over different healing cycles; resistance change and recovery of notched and unnotched SW-b conductor films; photos of the PAA/F108 1/9 elastomer before being stretched, after being stretched to 500%, immediately after release, and 20 min after release (PDF)

Movies showing the elongation of PAA/PEO 1/9 and PAA/F108 1/9 blends (Movies S1 and S2) (AVI) (AVI)

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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