

Facile and Large-scale Fabrication of Self-crimping Elastic Fibers for Large Strain Sensors

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Electronic Supplementary Information

Abstract Stretchable conductive fibers offer unparalleled advantages in the development of wearable strain sensors for smart textiles due to their excellent flexibility and weaveability. However, the practical applications of these fibers in wearable devices are hindered by either contradictory properties of conductive fibers (high stretchability versus high sensing stability), or lack of manufacturing scalability. Herein, we present a facile approach for highly stretchable self-crimping fiber strain sensors based on a polyether-ester (TPEE) elastomer matrix using a side-by-side bicomponent melt-spinning process involving two parallel but attached components with different shrinkage properties. The TPEE component serves as a highly elastic mechanical support layer within the bicomponent fibers, while the conductive component (E-TPEE) of carbon black (CB), multiwalled carbon nanotubes (MWCNTs) and TPEE works as a strain-sensitive layer. In addition to the intrinsic elasticity of the matrix, the TPEE/E-TPEE bicomponent fibers present an excellent form of elasticity due to self-crimping. The self-crimping elongation of the fibers can provide a large deformation, and after the crimp disappears, the intrinsic elastic deformation is responsible for monitoring the strain sensing. The reliable strain sensing range of the TPEE/E-TPEE composite fibers was 160%–270% and could be regulated by adjusting the crimp structure. More importantly, the TPEE/E-TPEE fibers had a diameter of 30–40 μm and tenacity of 40–50 MPa, showing the necessary practicality. This work introduces new possibilities for fiber strain sensors produced in standard industrial spinning machines.

Keywords Conductive polyether-ester elastic fiber; Side-by-side bicomponent fiber; Self-crimping; Strain sensing

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INTRODUCTION

Stretchable and flexible sensors, a crucial element of wearable electronics, have extensive applications in smart textiles and garments, including human-motion detection, personalized health monitoring and human-machine interfaces.^[1–3] Conventional strain sensors fabricated from metals or semiconductors exhibit a limited deformation of less than 5% and are inherently rigid, prohibiting their use in wearable applications where the deformation can be as large as 55%.^[4] To fabricate strain sensors with large and steady deformation behavior, various approaches have been employed, including printing,^[5] vacuum filtration,^[6] spin-coating,^[7] dip-coating,^[8] casting,^[9] depositing^[10] and some other techniques. Although each of these methods appears to be effective for creating the flexible sensors by combining conductive nanomaterials with elastic

polymers, some disadvantages are also obvious, such as the complex process, high cost or lack of large-scale production capacity. Moreover, most strain sensors are planar-laminated constructs, while in use, they have to be attached to textiles by bonding or sewing. Due to difficulties in flexible integration with textiles, these sensors are actually uncomfortable for wearing. In contrast, fiber-based sensors can withstand mechanical deformations such as stretching, bending, folding and twisting and offer unparalleled advantages in weaving with traditional textiles.^[11–13] To create suitable fiber sensors for practical use, three basic properties of the fibers have to be garnered particular attention: (i) accommodation of high strain levels (> 50%)^[14] associated with complex human motions; (ii) good conductive stability and reversibility during stretch/release processes;^[15] and (iii) good processability for continuous large-scale production.

To date, a variety of stretchable fiber-based sensors based on the combination of a conductive filler (e.g., conductive polymers,^[16] metal and metal oxide particles,^[17] or carbon-based nanomaterials^[18–20]) and an elastic polymer matrix have been designed and prepared, such as poly(styrene- β -isobutylene- β -styrene)-poly(3-hexylthiophene) (SIBS-P3HT)

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fibers,^[21] silver nanowire/silver nanoparticle/styrene-butadiene-styrene (AgNW/AgNP/SBS) fibers^[22] and graphene oxide/polyurethane (GO/PU) fibers.^[23] Although significant progress has been achieved to date, most of the reported fiber-shaped sensors in the laboratory have not reached the level of practical application. Their commercialization is hindered because the properties of conductive elastic fibers under deformation, namely, conductivity stability and high stretchability, appear to be mutually exclusive. Seyedin *et al.*^[20] produced conductive elastomer polyurethane (PU) composite fibers with various nanocarbon fillers using wet spinning technology. This composite fiber-based strain sensor (at 4.8 wt% single-walled carbon nanotube (SWCNT) loading) showed the largest strain sensing range of 60%. He *et al.*^[24] evaluated the real-time mechanical feedback of TPU/multiwalled carbon nanotube (MWCNT) fibers for some small deformation detection of human motion. Wang *et al.*^[25] developed a strain sensor based on conductive poly(styrene-butadiene-styrene)/few layer graphene (SBS/FLG) composite fibers through a wet-spinning process. Although the workable strain range of the SBS/FLG fibers was reported to be as large as 110%, an obvious residual deformation of approximately 10% was observed after 50% strain was released, which would affect the stability of the strain sensing response. Bautista-Quijano *et al.*^[26] developed a fiber-shaped strain sensor based on melt-spun polycarbonate (PC)/MWCNT fibers, which exhibited a lower sensing range of 6% strain. The fabrication of conducting elastic fibers using spinning can be easily and efficiently scaled up to produce strain sensing fibers, yet imparting electrical properties in elastic polymer fibers while maintaining the stretchability has been a challenge. The reason is that introducing a high loading of conductive fillers often results in deterioration of spinnability or can lead to fibers with low stretchability, which are not suitable for large strain applications.^[27] By contrast, coating or depositing conductive materials onto the fibers was considered as a possible solution to improving the conductivity of fibers with the addition of a lower content of conductive fillers. Wang *et al.*^[28] produced a strain sensor based on polypyrrole (PPy)-coated Lycra fibers and the sensing range was found to be up to a strain of 50%. Zhang *et al.*^[29] reported a sheath-core graphite/spandex fiber and a graphite/silk fiber made by rod-coating, showing workable strain sensing ranges of approximately 30% and 15%, respectively. Liao *et al.*^[30] prepared a stretchable strain sensor consisting of ZnO nanowires and polyurethane fibers using hydrothermal growth, showing a tolerable strain up to 150%. Nonetheless, some deficiencies of the coated fibers are also obvious. The poor adhesion and mechanical property mismatch between the fiber substrate and the conductive coating layer often result in the degradation of the sensing response, especially for applications requiring large strains or numerous cycles.^[4,27] In fact, considering the performance shortcoming of these strain sensing fibers prepared by conventional processing technology, novel stretchable fiber-shaped sensors have gained considerable research interest and have been designed in a variety of emerging technologies, including “microfibers with intrinsic microbeads”,^[31] “three-dimensional interpenetrating Ag nanowires/polyolefin elastomer nanofi-

brous yarn”,^[32] “hierarchically buckled sheath-core fibers”^[33] and so on. Moreover, although various fibrous sensors have been demonstrated to exhibit excellent conductivity and high mechanical stretchability, many of the methods for fabricating the fiber-shaped sensors mentioned above are complicated, time-consuming and uncontrollable. Thus, the development of a cost-effective, mass-production approach for the fabrication of highly stretchable and durable fiber-based strain sensors with a stable response would be a valuable innovation.

In this study, we demonstrated a self-crimping fiber strain sensor based on a thermoplastic polyetherester elastomer (TPEE) to simultaneously attain high conductivity stability and high stretchability through a scalable bicomponent melt-spinning process. The objective of spinning such fibers is to overcome the limitations (tenacity or elastic loss) encountered during conventional single component spinning. The two components, TPEE and conductive TPEE (E-TPEE, containing CB and MWCNTs as fillers), were fed to a single spinneret hole split by a septum that channelled the two components into a side-by-side arrangement. The TPEE component serves as a highly elastic mechanical support layer, while the E-TPEE component works as a strain-sensitive layer. The bicomponent conductive fiber concept has been proven to be an effective approach for industrial-scale production.^[34,35] In particular, the side-by-side TPEE/E-TPEE bicomponent fibers possess a self-crimping structure, relying on the difference in shrinkage between the two polymers.^[36,37] Compared with conventional elastic fibers, the TPEE/E-TPEE bicomponent fibers not only exhibit intrinsic elasticity from the TPEE matrix, but also form elasticity due to the self-crimping structure. The crimp deformation of the TPEE/E-TPEE bicomponent fibers can provide a large deformation, and after the crimp disappeared, the intrinsic elastic deformation was responsible for monitoring the strain sensing. The crimp contraction of the fibers is capable of being designed freely either by composition ratio or by process conditions,^[38] which offers opportunities to adjust the strain sensing range. In current study, the mechanism of crimp structure formation of the TPEE/E-TPEE fibers was revealed, and the strain sensing behavior at large deformation was comprehensively evaluated, laying the foundation for regulating the structure and performance of the fibers. This research could provide useful information for the large-scale development of flexible fiber-based strain sensing materials.

EXPERIMENTAL

Materials

Conductive carbon black (CB, Printex XE 2B) was supplied by Evonik Degussa with an average particle size of 30 nm and a specific surface area of approximately 900 m²/g. Multiwalled carbon nanotubes (MWCNTs, TNIM1), with a diameter of 5–15 nm, length of 10–30 μm and purity of 95 wt%, were purchased from Chengdu Organic Chemicals Co., Ltd. (Chinese Academy of Sciences, Chengdu, China). Thermoplastic copolyether-ester elastomer (TPEE) (HP4001) composed of poly(butylene terephthalate) (PBT) as hard segments and

poly(tetramethyleneglycol) (PTMG) as soft segments was used as the polymer matrix and was kindly supplied by Shanghai Etonpolymer Co., Ltd. The hard/soft segment mass ratio was 4:6 in this copolymer. The intrinsic viscosity ($[\eta]$) of the TPEE was 1.69 dL/g, which was measured using a phenol/tetrachloroethane (1:1 in mass ratio) mixed solvent at 25 °C.

Fraction of TPEE/E-TPEE Bicomponent Fibers

The TPEE polymer compounds were homogeneously mixed using a twin-screw extruder (SHJ-20B) to produce conductive TPEE masterbatches (E-TPEE) with 20 wt% CB and 1 wt% MWCNTs (Fig. 1a). The content of CB and MWCNT was determined by considering the electrical conductivity and spinnability of E-TPEE component. Here, the mixture was extruded at a temperature of 230 °C. Before extrusion, the TPEE powder (~35 mesh in size) was premixed with CB and MWCNTs by a home-mixer at 500 r/min to improve the dispersion of the conductive fillers.

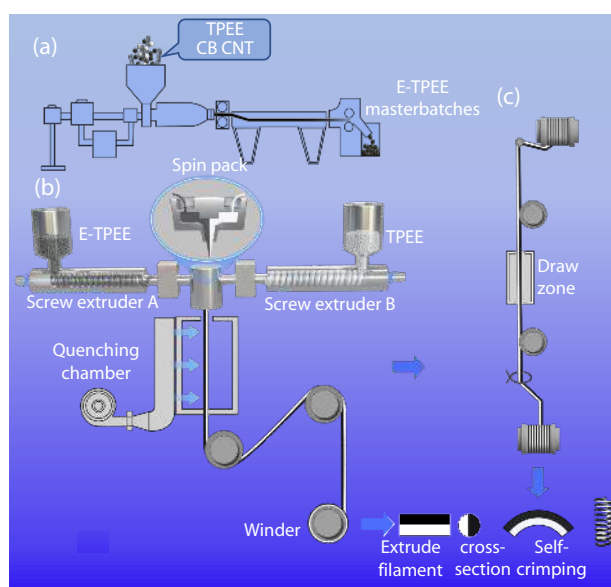


Fig. 1 Schematic of drawing of (a) fabrication of E-TPEE masterbatches, (b) side-by-side bicomponent melt spinning, and (c) heat-stretching.

The TPEE/E-TPEE bicomponent fibers were produced by using a bicomponent melt-spinning machine (ABE $\phi 25 \times 2$, FUJI FILTER, Japan) (Fig. 1b). In this investigation, two individual single-screw extruders extruded TPEE, E-TPEE and their conjugated parts separately into the conjugated spin-pack, which had a side-by-side conformation. The extruded as-spun bicomponent fibers were taken up at a speed of 500 m/min. Subsequently, the as-spun fibers were subjected to heat stretching (Fig. 1c). The final TPEE/E-TPEE bicomponent fibers with a diameter of 35 μm exhibited self-crimping. Four different TPEE/E-TPEE composition ratios (50:50, 60:40, 70:30 and 80:20) in the bicomponent fibers were employed to regulate the self-crimping structure of the fibers, which were denoted as TPEE50/E-TPEE50, TPEE60/E-TPEE40, TPEE70/E-TPEE30 and TPEE80/E-TPEE20, respectively. To reveal the mechanism of crimp structure formation of the TPEE/E-TPEE fibers, pure monocomponent TPEE and E-TPEE fibers were also produced

under the same conditions to evaluate the structural variations of each component in the bicomponent fibers.

Characterization

The crimp features of the TPEE/E-TPEE bicomponent fibers were investigated using a digital camera. The cross-section of the bicomponent fibers was observed using an optical microscope (8XB-PC, Shanghai Optical Instrument Factory). The TPEE/E-TPEE bicomponent fibers were cryogenically broken by a fiber slicer under liquid nitrogen prior to observation. The dispersion of conductive fillers within the fibers was characterized by scanning electron microscopy (SEM, Hitachi S-3000N).

The mechanical behavior of the TPEE/E-TPEE fibers was measured using a universal testing machine (KQL, Shenzhen Kaiqiangli Test Instrument Co., Ltd.) with a gauge length of 50 mm and an extension rate of 20 mm/min. A pretension of 10^{-5} cN/dtex was applied to the samples without causing tangling of the fibers, and the fibers still exhibited self-crimping with different degrees of crimpness. At least 20 samples were tested for each sample, and the average values for the tenacity and elongation at break were calculated.

The thermomechanical properties of TPEE/E-TPEE composite fibers were determined on a thermal analyzer (TMA/SS 7100, Hitachi) over a temperature range from 30 °C to 180 °C at a rate of 5 °C/min. A single fiber was clamped into the sample holder with a small initial stress in order to keep the fiber straight. This initial stress was approximately 3 MPa. Two different modes were used in this analysis: (1) measurement of the change in fiber length at constant stress and (2) measurement of the change in stress at constant fiber length.

The conductivity of the bicomponent fibers was measured by a two-point method using an electric resistance tester (XQ-1A, Shanghai Xinxian Instrument Co., Ltd.). Copper tape was applied on the fiber ends as electrodes. The resistivity can be calculated using the resistance by the following formula: $\rho = (\pi R d^2)/4l$, where R is the resistance of the sample, d is diameter of the fiber, and l is the length of the fiber. The strain response sensing test was performed by loading the fiber samples on a KQL universal test machine with a gauge length of 20 mm and the resistance change during stretching using a high resistivity meter (TH2684A, Changzhou Tonghui Electronics Co., Ltd.) was measured simultaneously. The electric contacts were obtained by copper tape attached to the fiber and insulated from the tensile test machine frame. Ten extension-retraction cycles were conducted at a constant extension rate of 10 mm/min in order to investigate the strain sensing reproducibility of the fibers.

RESULTS AND DISCUSSION

Morphology of TPEE/E-TPEE Composite Fibers with Various Composition Ratios

The TPEE/E-TPEE composite fibers were composed of polyether-ester elastomer components and polyether-ester elastomer components with 20 wt% CB and 1 wt% MWCNTs as conductive fillers (E-TPEE) and fabricated using a facile bicomponent melt-spinning process. The cross-section, surface and self-crimping morphologies of TPEE/E-TPEE composite fibers with various composition ratios were observed, as shown in Fig. 2. Longitudinally, the TPEE component and E-TPEE component

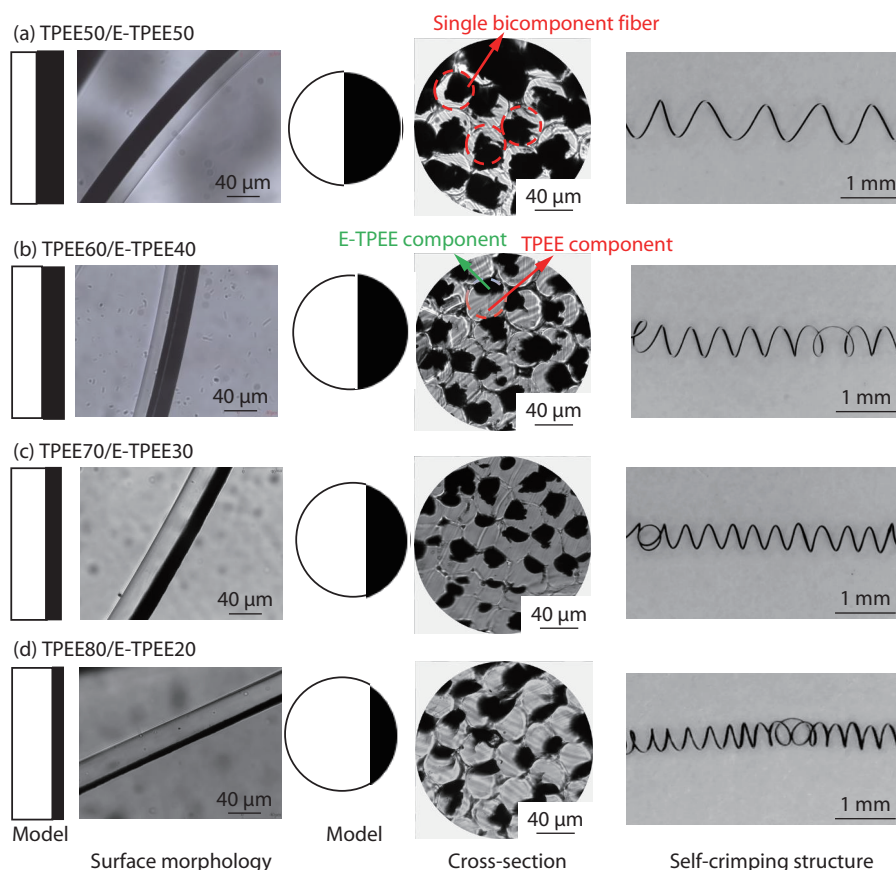


Fig. 2 Morphology of TPEE/E-TPEE composite fibers with various composition ratios.

within the fibers appeared to be proportionally arranged in a side-by-side parallel configuration corresponding to the composition ratio. Theoretically, the TPEE/E-TPEE composite fibers should also present a straight interface in the cross-section, which can exhibit the best crimp potential, as reported by Denton.^[39] In fact, some irregular interfaces occurred between the two components, as shown in Fig. 2. This phenomenon is mainly due to the difference in viscosity between two individual polymers when producing a bicomponent fiber, which can cause serious migration and deform the interface.^[36] In other words, the high-viscosity E-TPEE component with large surface tension tended to be covered by the low-viscosity TPEE component. Even then, the interface of the TPEE/E-TPEE composite fibers can still be adjusted by changing the composition ratios. As such, TPEE/E-TPEE composite fibers with different crimping structures were obtained. When the ratio of TPEE/E-TPEE components was 5:5, the composite fibers exhibited a large and sparse crimp structure; that is, the curl radius and pitch of the crimp structure were relatively larger than those of the other composite fibers. With increasing TPEE component content, the curl radius and pitch of the fibers decreased, showing a small and dense crimp structure. The reason for the crimp structure formation of the TPEE/E-TPEE composite fibers will be explained in detail in the following section.

Mechanical Properties of TPEE/E-TPEE Composite Fibers with Various Composition Ratios

As previously mentioned, a high content of carbon fillers in

conductive elastic fibers may lead to the loss of certain fiber characteristics such as tenacity and elasticity, affecting their application. Taking the monocomponent fibers as an example (Fig. 3a), the maximum stress achieved in the TPEE monocomponent fibers was approximately 100 MPa, and the elongation at break reached 200%. However, it can be observed that the stress and ultimate elongation at break of the E-TPEE monocomponent fibers with the addition of conductive carbon fillers were obviously reduced to 25 MPa and 40%, respectively. In contrast, it can be observed clearly that the stress-strain curves of the TPEE/E-TPEE composite fibers are different from those of the monocomponent fibers. The curve can be divided into two regions (Fig. 3b): (1) crimp extension stage, where a large deformation can be observed under the action of low load, and the largest deformation range can be adjusted from 160% to 240% depending on the composition ratios of the fibers; and (2) the natural or inherent stretch deformation stage, where after the crimp disappears, the stress curve demonstrates a prominent dependence of the stress on the strain, and the strain sensing response may be detected at this stage. Seen in this light, the strain sensing range of the conductive elastic fibers can be regulated by the tunable crimp structure. In addition, it is worth mentioning that the TPEE component serves as a highly elastic mechanical support layer within the composite fibers. Thus, the tenacity of the conductive composite fibers can still be maintained at approximately 40–50 MPa, which is much higher than that of the E-TPEE monocomponent fibers. In other words, the TPEE/E-TPEE

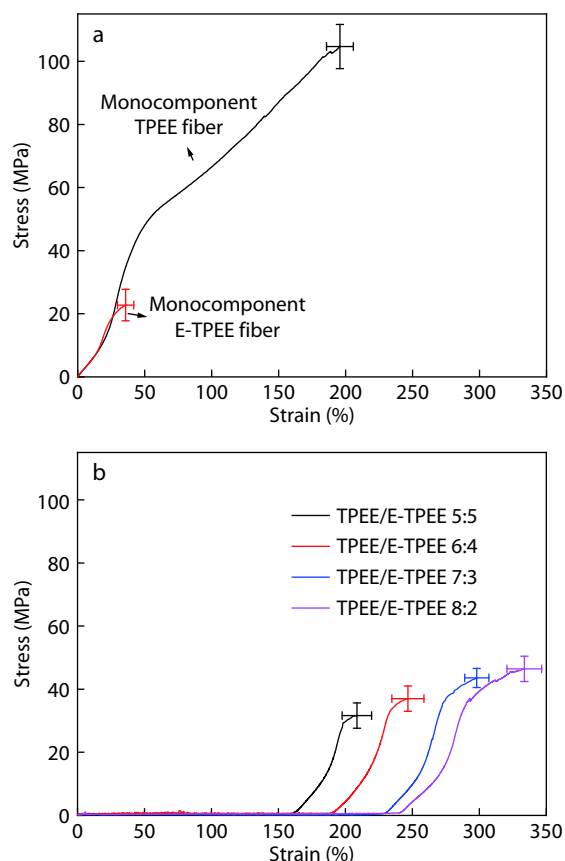


Fig. 3 Stress-strain curves of monocomponent fibers (a) and TPEE/E-TPEE composite fibers with various composition ratios (b).

conductive composite fibers have more practical values.

Analysis of the Crimp Formation Mechanism of TPEE/E-TPEE Composite Fibers

As is well known, the thermal shrinkage difference between the two components with side-by-side composite fibers is the key factor in crimp formation. In fact, it is difficult to quantitatively characterize the structure and performance of each component within the composite fibers. To freely regulate the self-crimping structure of the fibers, it is necessary to reveal the formation mechanism of the TPEE/E-TPEE composite fibers. Therefore, TPEE and E-TPEE monocomponent fibers as model fibers were produced with the same processing parameters as those of the composite fibers. Then, thermomechanical analysis of the TPEE and E-TPEE monocomponent fibers and TPEE/E-TPEE composite fibers was conducted, as shown in Figs. 4 and 5. The thermal shrinkage strain was developed in the monocomponent fibers and composite fibers under tension close to zero at a heating rate of 5 °C/min. From Fig. 4, two different shrinkage processes (a negative change in the sample length) are observed. The first shrinkage process occurs at temperatures ranging from 50 °C to 110 °C (Fig. 4a), which may reflect segmental motion in the noncrystalline region of the polymers. The higher the degree of orientation of noncrystalline molecules is, the larger the shrinkage of the fibers is. As the temperature increases, the second shrinkage process can be observed and can be termed “relative elongation” compared with the first stage. The observation seems to imply that the molecular chains have

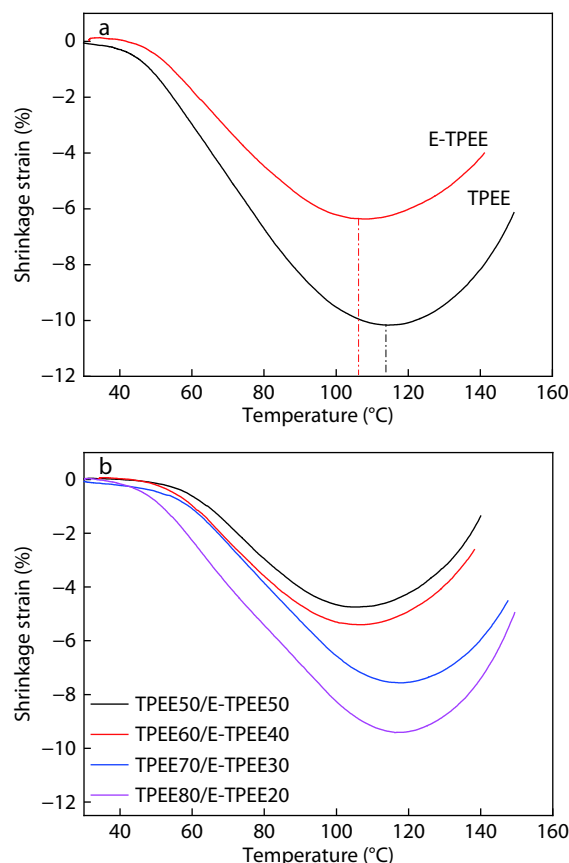


Fig. 4 Thermal shrinkage curves of monocomponent fibers (a) and TPEE/E-TPEE fibers with various composition ratios (b).

been fully relaxed and have less orientation after the first stage, which subsequently yields a relative elongation even under slight pretension. Moreover, the shrinkage of the monocomponent TPEE fibers is greater than that of the monocomponent E-TPEE fibers. The TPEE fibers achieve a maximum shrinkage value at approximately 113 °C, which is 6 °C higher than that of the E-TPEE fibers. Based on this result, it is reasonable to deduce that the molecular chains packed within the E-TPEE fibers are characterized with a lower orientation and less ordered structure than those of TPEE fibers, as confirmed by wide angle X-ray scattering (WAXS) analysis (Fig. S1 in the electronic supplementary information, ESI). For the TPEE/E-TPEE composite fibers, the thermal shrinkage curves show trends similar to those of the monocomponent fibers (Fig. 4b). The composite fibers show larger shrinkage with increasing TPEE component content, and the peak temperature corresponding to the largest shrinkage value shifts to a higher temperature.

Fig. 5 depicts the thermal shrinkage stress appearing in the monocomponent and composite fibers under a fixed sample length at the same heating rate. The variation trend of the shrinkage stress behavior corresponds to the shrinkage strain behavior observed in Fig. 4. As expected, the TPEE component within the fibers has a larger shrinkage stress and peak temperature than the E-TPEE component. The higher the content of TPEE within the composite fibers is, the larger the shrinkage stress is.

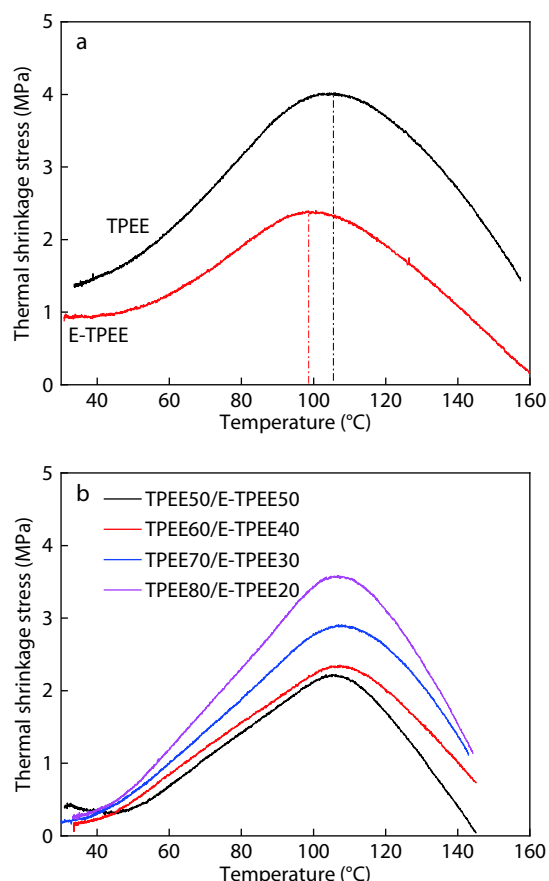


Fig. 5 Thermal shrinkage stress curves of the monocomponent fibers (a) and TPEE/E-TPEE fibers with various composition ratios (b).

From this point, it is reasonable to state that although the two components within the composite fibers will shrink simultaneously when subjected to heat treatment, the E-TPEE component exhibits a larger shrinkage modulus than the TPEE component does due to the addition of rigid conductive carbon materials. As is analyzed above, the shrinkage behavior of the TPEE component is greater than that of the E-TPEE component during heat treatment and has an obvious temperature difference. When the E-TPEE component within the composite fibers reached the maximum shrinkage, the tendency of the TPEE components to continue shrinking will be hindered by the E-TPEE components, leading to an asymmetric residual stress distribution in the radial direction of the

composite fibers. Thus, these TPEE/E-TPEE composite fibers will curl, where the TPEE component is arranged on the inner side of the turning point and the E-TPEE component is on the outside of the turning point within the composite fibers (Fig. 6). This phenomenon is consistent with the TMA results.

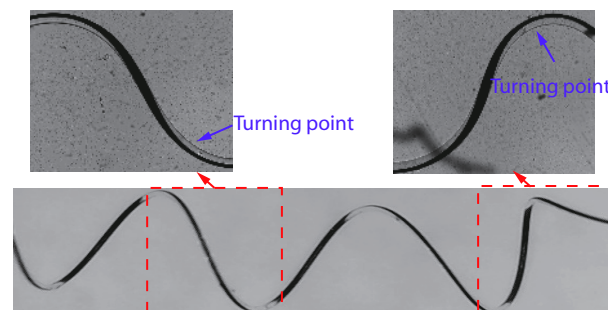


Fig. 6 Crimp structure of TPEE/E-TPEE composite fibers.

Electrical Properties of TPEE/E-TPEE Composite Fibers

To be used as stretchable strain sensors, the TPEE/E-TPEE composite fibers should have excellent electronic properties. The conductive network structure within the fibers was investigated by SEM, as shown in Fig. 7. Compared to smooth TPEE component (Fig. 7b), the spherical carbon black particles are homogeneously dispersed throughout the E-TPEE component and overlap to form a conductive network path (Fig. 7c). Unfortunately, it is difficult to distinguish the carbon nanotubes clearly because the content of carbon nanotubes (1 wt%) is much lower than that of carbon black (20 wt%) in the matrix.

The electrical resistivity of the TPEE/E-TPEE composite fibers was observed to be approximately 10^2 – 10^4 Ω ·cm and measured using the two-point probe method, as shown in Fig. 8. A slight increase in the resistivity of TPEE/E-TPEE fibers can be observed with increasing TPEE component content. Nevertheless, these composite fibers can still be used as strain sensors.

To characterize the strain response sensing behaviors, the relative resistance change as a function of the applied strain was measured at a strain rate of 10 mm/min. Fig. 9 shows the curve of the relative changes in the resistance ($\Delta R/R_0$) versus strain of the TPEE/E-TPEE composite fibers, $\Delta R = R - R_0$, where R_0 and R are the initial resistance and real-time resistance during stretching, respectively. Note that the TPEE/E-TPEE com-

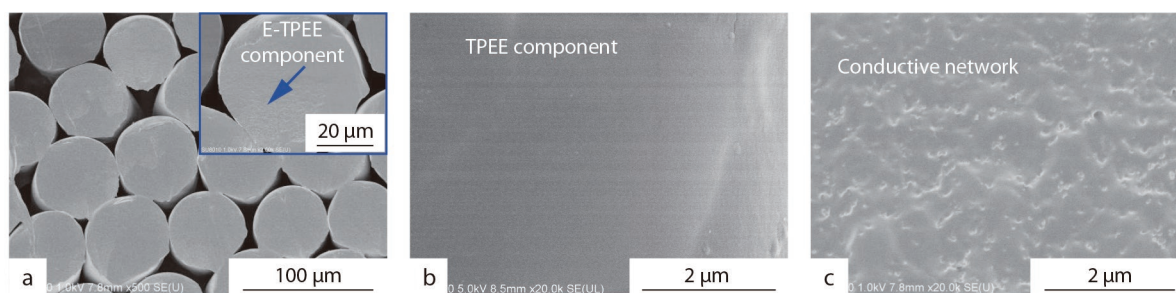


Fig. 7 SEM images of the dispersion of conductive fillers within the TPEE/E-TPEE composite fibers: (a) cross-section of TPEE/E-TPEE fibers, (b) morphology of TPEE component, and (c) dispersion of conductive carbon fillers.

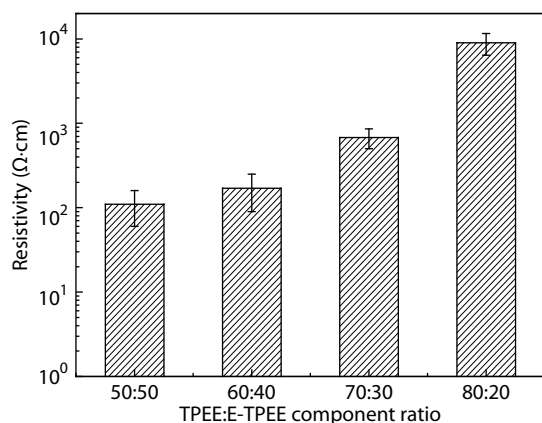


Fig. 8 Electrical resistivity of TPEE/E-TPEE composite fibers.

posite fibers with different component ratios showed three different change rules in resistance under strain until the sensor failed. The TPEE/E-TPEE fiber sensors exhibited time-invariant resistance at the initial stages of deformation corresponding to crimp extension of the fibers, which has less effect on the conductive network within the fibers. Notably, the crimp extension range of the composite fibers can be adjusted by changing the ratio of each component or by adjusting spinning parameters such as the heat stretching temperature or ratio.^[40] Here, some primary research on the relationship

between the component ratio and crimp structure was explored, and crimp elongation could be regulated within the strain range of 160%–240%, laying a good foundation for a large strain sensing response. After the crimp is fully straightened, the TPEE/E-TPEE composite fibers displayed a negative resistance variation within a 30% strain range during intrinsic elastic deformation, whereas a negative-to-positive resistance variation was observed at an intrinsic elastic strain beyond 30%. The particular strain sensing behavior is mainly attributed to the dispersion of conductive carbon particles as well as their spatial arrangement. The plausible mechanism of the strain sensing of TPEE/E-TPEE composite fibers is schematically shown in Fig. 10. Because the E-TPEE components contain 20 wt% carbon black and 1 wt% MWCNTs as conductive fillers, it can be deduced that the conductive network is formed mainly by the connection of higher concentrations of CB aggregates at the initial state. Subsequently, the high-aspect-ratio MWCNTs reorient at an intrinsic elastic deformation lower than 30% and play the role of bridging or linking the gap between CB to form new conductive paths, resulting in a peculiar negative response. At much higher strains (intrinsic elastic deformation exceeding 30%), destruction of the contact points of aligned MWCNTs and CB significantly dominates, leading to the breakage of conductivity pathways. Thus, the relative resistance exhibits an obvious increase from a negative to a positive resistance variation.

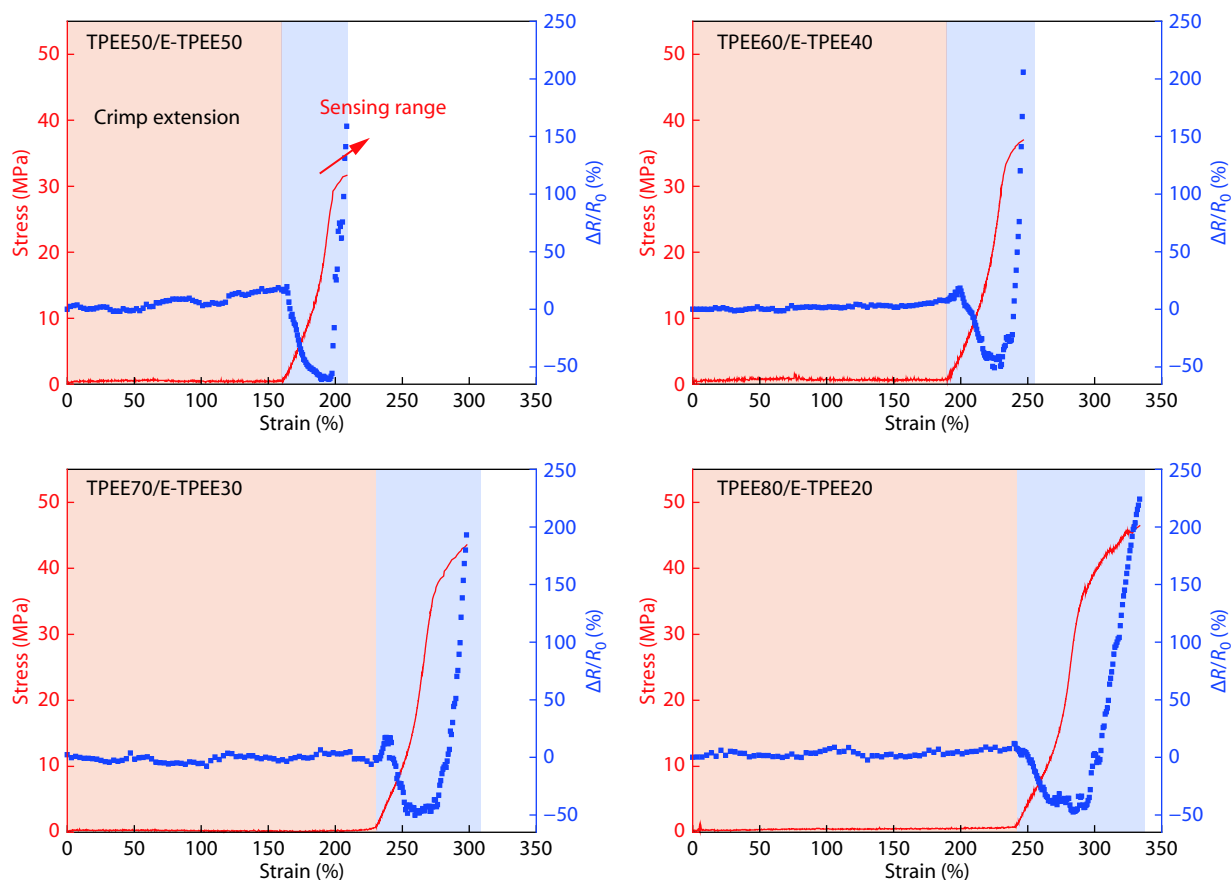


Fig. 9 Strain-sensing characterization of TPEE/E-TPEE composite fibers with various component ratios during the stretching process.

For practical applications, there is no doubt that the crimp morphology of the TPEE/E-TPEE fibers can be used to adjust the deformation range of the fibers. The strain sensing behavior of the TPEE/E-TPEE composite fibers during the stretch/release cycle process was also investigated with an intrinsic elastic deformation between 0% and 30% strain, where the fibers only exhibit a monotonic variation in the resistance (Fig. 11). It was observed that the relative resistance decreased with increasing intrinsic elastic deformation and increased with decreasing intrinsic elastic deformation. However, the resistivity of the TPEE/E-TPEE composite fibers is not fully recoverable within the experimental time scale under the selected strain conditions, which is known as elec-

tromechanical hysteresis. After a stretch/release cycle, the final recorded resistance is slightly larger than the initial resistance before testing. This difference is mainly caused by the mechanical hysteresis of the TPEE matrix and the destruction of the unstable conductive network structure. Notably, the electromechanical hysteresis is less dependent on the component ratio of the composite fibers but is affected by the content of the conductive filler and the interaction between the fillers and TPEE. Therefore, determining how to design conductive network structures will be a research focus in our future endeavors.

To evaluate the dynamic durability and reliability of the TPEE/E-TPEE composite fibers, the dynamic strain sensing be-

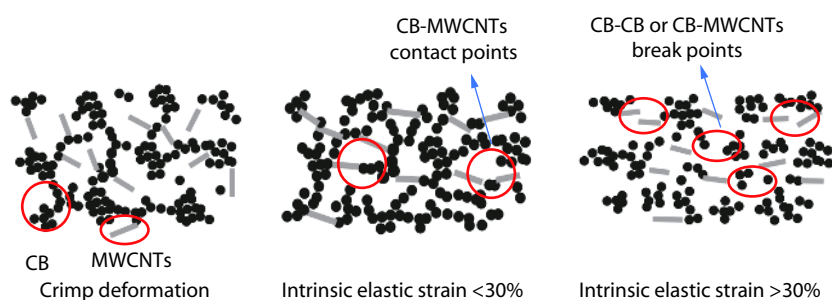


Fig. 10 Schematic presentation of the morphologies of the CB and MWCNT hybrid fillers within the composite fibers showing the connecting pathways of electron transfer.

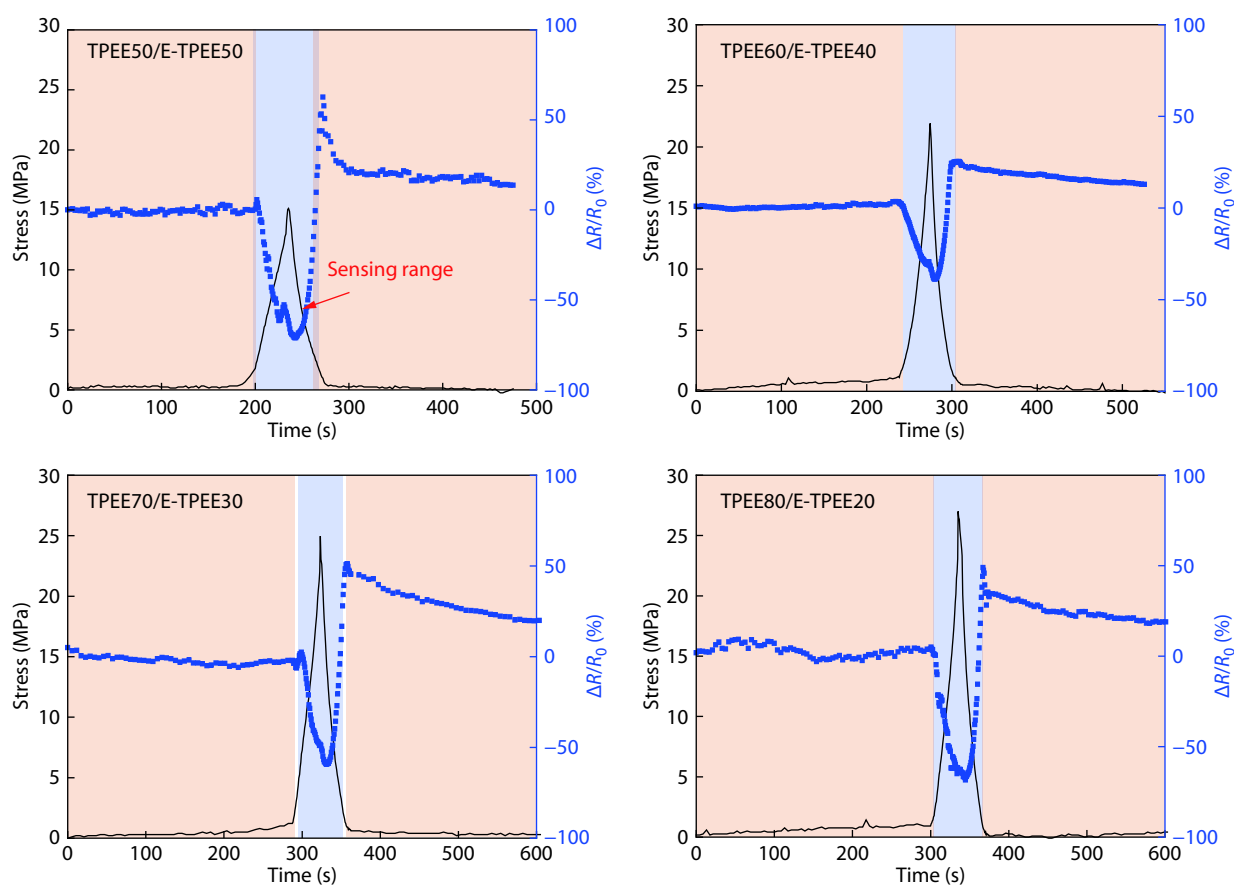


Fig. 11 Strain sensing behaviors of TPEE/E-TPEE composite fibers with various component ratios during the stretch/release process.

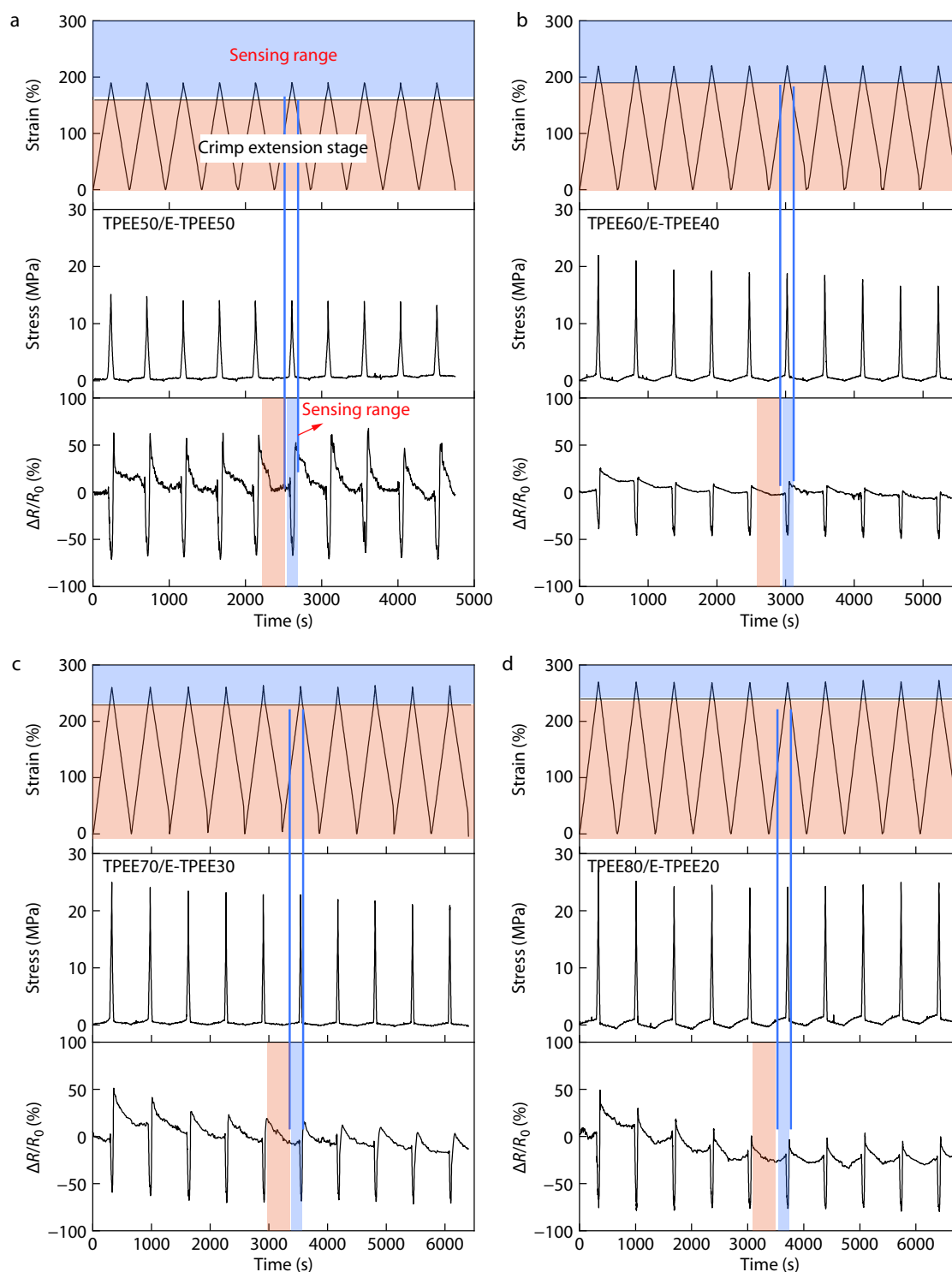


Fig. 12 Strain sensing behaviors of TPEE/E-TPEE composite fibers with various component ratios during 10 stretch/release cycles: (a) TPEE50/E-TPEE50, (b) TPEE60/E-TPEE40, (c) TPEE70/E-TPEE30 and (d) TPEE80/E-TPEE20.

havior was studied with several stretch/release cycles, as shown in Fig. 12. Even though hysteresis was observed at the selected strain, the TPEE/E-TPEE composite fiber strain sensor showed a stable and reliable response to the applied tensile strain. The relative resistance values of the TPEE/E-TPEE com-

posite fibers after each cycle are close to the initial values, suggesting that the conducting particles could fully realign and tend to restore the initial conducting network structure during the crimp recovery process. That is, the resistance hysteresis has little effect on the strain sensing reliability of the

composite fibers. Therefore, such conductive TPEE/E-TPEE composite fiber strain sensors are designable and have potential applications in monitoring large deformations or motions.

CONCLUSIONS

In summary, novel stretchable conductive TPEE/E-TPEE composite fibers were fabricated in a cost-effective manner using the side-by-side bicomponent melt-spinning method. The TPEE component serves as a highly elastic mechanical support layer within the composite fibers, while the E-TPEE component can enable a strain response. The TPEE/E-TPEE composite fibers exhibit three-dimensional self-crimping elasticity and intrinsic entropy elasticity. The crimp elongation of the fibers can provide large deformation. After the crimp disappears, the fiber exhibits effective strain sensing behavior in the further intrinsic elastic deformation stage. The strain sensing response range of the composite fibers can be adjusted by changing the crimp structure of the fibers, which can be regulated by the component ratios. In addition, the TPEE/E-TPEE composite fibers show a highly stable and reliable strain response and have promising prospects in practical production.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-021-2560-1>.

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