

Mechano-responsive hydrogen-bonding array of thermoplastic polyurethane elastomer captures both strength and self-healing

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Article

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Abstract

Self-repairable materials strive to emulate curable and resilient biological tissue; however, their performance is currently insufficient for commercialization purposes because mending and toughening are mutually exclusive. Here, we report a carbonate-type thermoplastic polyurethane elastomer that self-heals at 35 °C and is as strong as footwear elastomers. This elastomer exhibits the highest tensile strength to date (43 MPa). Distinctively, it has abundant carbonyl groups in soft-segments and is fully amorphous with negligible phase separation due to poor hard-segment stacking. It operates in dual mechano-responsive mode through a reversible disorder-to-order transition of its hydrogen-bonding array; it heals when static and toughens when dynamic. In static mode, non-crystalline hard segments promote dynamic exchange of disordered carbonyl hydrogen-bonds for self-healing. The amorphous phase forms stiff crystals when stretched through a transition that orders inter-chain hydrogen bonding. The phase and strain fully return to the pre-stressed state after release to repeat healing process.

Introduction

Self-healing materials that autonomously and repeatedly repair physical damage through dynamic physical or chemical bonds¹⁻⁷ have gained significant levels of attention in a variety of material fields, including automobile components^{8,9}, electronics¹⁰⁻¹⁴, robotics^{15,16}, and healthcare devices¹⁷⁻²⁰. However, the trade-off between mechanical and healing performance is the biggest hurdle that these materials face and need to overcome. The high chain rigidity, entanglement, and crystallinity required for mechanical strength conflict with the high diffusibility and exchange of dynamic bonds required for repairing damage²¹⁻²⁴. Consequently, materials that autonomously heal at ambient temperature exhibit mechanical performance that is unsatisfactory for industrial commercialization.

In contrast, biological tissue is not only able to efficiently self-repair, but is also very tough and resilient^{25,26}. The “secrets” of some biological mechano-responsive processes that toughen biomaterials have recently been unveiled, but such insight remains undiscovered or undeveloped for man-made self-healing materials^{27,28}. For example, the egg-capsule wall of a channeled whelk effectively absorbs shock with a high degree of reversible extensibility and stiffness²⁹; its constituent proteins undergo reversible structural α -helix to β -sheet transitions with internal-energy changes when loaded. After the removal of stress, energy relaxation results in the recovery of a high degree of strain. As another example, the toughening and shape memory of spider silk is the result of the arrangement and density of the intermolecular hydrogen (H)-bonds in silk crystals that are tuned by the spinning rate from the spider’s secretion gland³⁰⁻³².

Herein, we report a self-healing carbonate-type thermoplastic polyurethane (TPU) elastomer with the highest concurrent ultimate tensile strength (UTS) reported to date (43 MPa) for a self-healing “elastomer” that functions at ambient temperature; this TPU even outperforms a commercial TPU used for a footwear component³³⁻³⁸. Basically, the rich carbonyl groups of the carbonate soft segments form

H-bonds. As opposed to a typical TPU, its hard segments are poorly stacked, thereby providing a fully amorphous phase as well as poor phase separation.

Mechano-responsive H-bond biomimicry involving the unique characteristics of the respective hard and soft segments is the key to the unprecedented superior performance of this material. The H-bonding array of carbonyl groups undergoes a reversible structural change upon external stress. In static mode, the amorphous phase enables the segmental swapping of H-bonds and the dynamic formation of aromatic disulfides, which enables self-repair in the absence of stress, with molecular flow retarded due to the abundant carbonyl H-bonds that increase the elastic modulus. Under strain, the amorphous phase is transformed into a rigid metastable crystal where ordered H-bonds form between stretched chains in order to endure heavy loads. After removal of the stress, the metastable crystal returns to the amorphous phase, with its shape and strain fully recovered, and is immediately available for self-healing.

Results

Preparing a strong self-healing elastomer that functions at ambient temperature

The self-healing TPU referred to as **C-IP-SS** was synthesized from poly(hexamethylene carbonate) diol (C, a carbonate-type aliphatic macrodiol) as the soft segment, asymmetric alicyclic isophorone diisocyanate (IP) as the hard segment, and an aromatic disulfide (SS) as the chain extender (Fig. 1a and Supplementary Fig. 1)^{39–44}. SS metathesis drives intrinsic self-healing at room temperature^{45,46}. Our previous self-healing TPU (referred to as **E-IP-SS**), which contains ether-type macrodiol (E), IP, and SS units⁴⁷, was used as the control. Both self-healing TPUs have equal (15 wt%) macrodiol compositions and number-average molecular weights (M_n s) of 1 kg mol^{-1} (Supplementary Figs. 2–6 and Supplementary Table 1). A commercial TPU (**Es-MD**) containing ester-type macrodiol (Es) and methylene diphenyl diisocyanate (MD) units was used as a non-self-healable control. The weight-average molecular weights (M_w s) of **C-IP-SS**, **E-IP-SS**, and **Es-MD** were measured to be 24, 46, and 99 kg mol^{-1} , respectively.

Interestingly, **C-IP-SS** exhibited significantly superior mechanical properties compared to other self-healing materials. The tensile properties of the three types of TPU film prepared by solvent casting were examined. Prior to this study, **E-IP-SS** exhibited the highest toughness (26.9 MJ m^{-3}) and UTS (6.8 MPa) among self-healing materials that function at ambient temperature (Fig. 1b). Nevertheless, its tensile performance is trivial compared to that of **Es-MD**, with a toughness and UTS of 115 MJ m^{-3} and 36 MPa, respectively. Although **C-IP-SS** has the lowest M_w among the TPUs, it has the highest UTS of 43 MPa and exhibits a 2.8-fold greater toughness (75 MJ m^{-3}) than **E-IP-SS** (Fig. 1c).

The outstanding tensile properties of **C-IP-SS** have little penalty on its self-healing efficiency. **C-IP-SS** films were cut in half, reattached, and then allowed to recover at $35 \text{ }^\circ\text{C}$ for varying amounts of time (Fig. 1b, c and Supplementary Table 2). UTS recoveries of 29, 39, 65, and 77% were observed after 1, 6, 24, and 48 h,

respectively. Notably, the UTS of the recovered **C-IP-SS** exceeded that of virgin **E-IP-SS** after only 1 h of self-healing; after 48 h, the recovered **C-IP-SS** is as strong as **Es-MD** (Fig. 1c, d and Supplementary Movie 1), and another cut and re-spliced film with a contact cut-area of 30 mm × 3 mm was able to readily lift a 10-kg weight (Fig. 1e and Supplementary Movie 2). Even after 1 min of recovery at room temperature (25 °C), a cut and re-spliced film with a contacted cut-area of 5 mm × 1 mm was able to withstand manual drawing and twisting (Fig. 1f and Supplementary Movie 3). According to the Ashby plot of UTS versus self-healing temperature for recently reported elastomers, previous tensile strengths did not exceed 20 MPa without the aid of light or a temperature above 40 °C (Supplementary Fig. 7 and Supplementary Table 3)^{9,21–24,34–40,42,43,47}.

Achieving Both Self-healing And Strength Through Reversible Structural Change

The breakthrough in the trade-off between self-healing and strength achieved for **C-IP-SS** is attributable to a dual mode of operation involving its mechano-responsive H-bonding array, with reversible strain-induced crystallization providing a major contribution. In the stress–strain curve for **C-IP-SS** (Fig. 1b), the concave upward trend is a clear sign of strain hardening. Figure 2a reveals that the tensile moduli (i.e., differential stress values) increase sharply with strain and are substantially different to those of **E-IP-SS** and **Es-MD**. **C-IP-SS** exhibits a more than 4.3-fold higher modulus than the other TPUs at 400% elongation, and becomes translucent due to the formation of crystallites, while the other TPUs remain relatively transparent (Fig. 2b, c and Supplementary Figs. 8 and 9). Interestingly, the original strain and transparency of **C-IP-SS** are fully recovered upon unloading (Supplementary Fig. 10 and Supplementary Movie 4); strain-induced crystallization upon loading is superficially incompatible with full recovery upon unloading; it cannot be explained either by the solid crystallization of semi-crystalline polymers or entropic elastomer elasticity because the former does not facilitate strain recovery, while the latter does not enable phase transition. Inspired by the recovery process of biomaterials, we deduce that rapid switching between the two individual internal structures drives the reversible deformation of **C-IP-SS** (Fig. 2d)⁴⁸.

The unusual strain-induced crystallization of **C-IP-SS** is strongly correlated with the reversible disorder-to-order switching of the mechano-responsive H-bonding array. Therefore, we separately investigated the internal H-bonding structures of **C-IP-SS** in its static and dynamic states by Fourier-transform infrared (FT-IR) spectroscopy (Fig. 3). As evidenced by differential scanning calorimetry (DSC), **C-IP-SS** is poorly microphase separated, with non-crystalline hard segments in the static state because the non-planar SS and IP moieties interfere with hard-segment stacking (Supplementary Fig. 11)⁴⁹. This behavior is unusual because typical TPUs have distinctly separated amorphous soft-domain and crystalline hard-domain microphases induced by the intermolecular stacking of mesogenic MD. The FT-IR spectrum of **Es-MD** shows an intense band at 1703 cm⁻¹ that corresponds to H-bonded urethane groups in the hard domain (Supplementary Fig. 12), and conventional carbonate-type TPUs that contain MD also exhibit two

dominant bands at approximately 1736 and 1699 cm^{-1} from their respective soft and hard domains^{41,50}. On the contrary, the FT-IR spectrum of **C-IP-SS** shows four different bands associated with carbonyl (C = O) groups that are assigned to ester groups that neighbor SS units (1645 cm^{-1}), those that are not H-bonded or are in disordered soft segments (1741 cm^{-1}), are involved in H-bonding between hard and soft segments (1718 cm^{-1}), and H-bonded between hard segments (1692 cm^{-1}) (Fig. 3a)^{51,52}. As a result, the band at 1718 cm^{-1} due to H-bonding between hard and soft segments is as strong as the band at 1692 cm^{-1} associated with H-bonding between hard segments. The -NH- units of each hard segment could form H-bonds with abundant soft segmental carbonyl groups⁵³. Therefore, in static mode, **C-IP-SS** has a relatively high degree of disorder with regard to its non-crystalline hard segments and the high concentration of H-bond-free carbonyl groups.

Uniaxial stretching in the dynamic state enhances the degree of H-bond ordering, leading to an increase in crystallinity and a decrease in the concentration of carbonyl groups that are not H-bonded, which is well-represented by a 2D gradient FT-IR map, in which the first derivative of the absorbance (A) as a function of the extension % (E) (i.e., dA/dE) is constructed in E versus wavenumber space (Fig. 3b)⁵⁴. The red and gray contours indicate positive and negative dA/dE , respectively. The strongest red and gray contour lines at 1718 and 1741 cm^{-1} , respectively, confirm that extension strengthens the adsorption band corresponding to H-bonding between hard and soft segments, but weakens the band associated with the absence of H-bonding or disordered soft segment, which is ascribable to the disorder-to-order transition of H-bonds between the laterally aligned stretched carbonate chains (i.e., crystallites) (Fig. 3c). As expected, the adsorption-band pattern fully returns to that of the original state after release. Thus, the mechano-responsive H-bonding structure undergoes array switching.

Rheology was used to explore whether or not the internal H-bonded structure affects the mechanics of **C-IP-SS** in static mode. Oscillating rheological testing at very low strain (1%) is a useful tool for investigating the static mode because it measures linear viscoelastic behavior. Each TPU was subjected to frequency sweep testing at 25 °C (Fig. 4a and Supplementary Fig. 13) to provide its complex viscosity at 0.05 rad s^{-1} ($\eta^*_{0.05}$), yield stress, and the slope of the Cole - Cole plot. In short, higher values of $\eta^*_{0.05}$ and yield stress, and lower Cole - Cole-plot slopes indicate that **C-IP-SS** is a more solid-like system^{20,55}.

The temperature-dependent loss tangents ($\tan \delta$) for the three TPUs were investigated in the 25–95 °C range (Fig. 4b). If $\tan \delta$ shows a decrease (or increase) by a standard value of unity, then the system exhibits solid-like (or liquid-like) behavior⁵⁶. In contrast to the $\tan \delta$ value of **E-IP-SS**, that of **C-IP-SS** remained below unity over the entire examined temperature range and was lowest near room temperature, which is a meaningful result because it reveals that a product made of **C-IP-SS** will be relatively safe from melting at high temperature. Moreover, **C-IP-SS** exhibited the highest Young's modulus (elastic modulus at a low tensile strain) of 15.5 MPa which is 11-, and 1.7-fold higher than those of **E-IP-SS**, and **Es-MD**, respectively (Supplementary Table 2). These data suggest that **C-IP-SS** is the most solid-like TPU among those studies owing to its rich carbonyl H-bonds, even though it has a four-fold lower M_w than **Es-MD**. As revealed by FT-IR spectroscopy, H-bonds are created between hard segments of **C-IP-SS** and all other hard

and soft segments to balance the disordered chains, while the H-bonds in **Es-MD** are relatively fixed between ordered hard segments, but are lacking between soft segments or disordered chains. Consequently, the former system exhibits a high degree of disorder while constructing a structure with a higher density of internal H-bonds than the latter.

As a motif for self-healing, the molecular process in static mode can be described by rheological master curves of storage (G') and loss (G'') moduli (Fig. 4c). A typical viscoelastic polymer shows four zones that are characterized by trends in G' and G'' (Fig. 4d) that are ordered as terminal, rubbery plateau, transition, and glassy zones⁵⁷. Comparing the two self-healable TPUs reveals that **E-IP-SS** only exhibits the first two zones, with a clear terminal region ($G'' > G'$). On the other hand, **C-IP-SS** shows three zones, from terminal to transition, with a dominant rubbery plateau region ($G' > G''$). These observations suggest that the chains in **C-IP-SS** experience a lower degree of molecular slips than those in **E-IP-SS**. As a quantitative parameter, the flow transition relaxation time (τ_f) was determined from the reciprocal frequency at the G'/G'' crossover between the terminal and rubbery zones, which was found to be > 2 years for **C-IP-SS** and 112 s for **E-IP-SS** (Fig. 4e), suggesting that **C-IP-SS** behaves more like a glassy solid than **E-IP-SS**; hence, chain-flow relaxation barely contributes to **C-IP-SS** healing on a reasonable time scale.

The key to **C-IP-SS** self-healing can be revealed from the segmental relaxation time (τ_s), which was calculated from its relaxation time curve at an angular frequency (ω) of 0.05 rad s^{-1} (Supplementary Fig. 14). The τ_s of **C-IP-SS** was calculated to be 8.5 s, very similar to that of **E-IP-SS** (7.4 s) (Fig. 4e). **C-IP-SS** self-healing is therefore a consequence of high segmental vibrations that enable the exchange of disordered H-bonds, and dynamic SS in the poorly microphase-separated system. We also note that classical chain-flow-mediated self-healing degrades mechanical properties, while segmental motion-driven self-healing minimizes the mechanical-property penalty. The difference between the molecular dynamics of flow transition and segmental motion is schematically illustrated in Supplementary Fig. 15.

X-ray tools can be used to trace the structural changes that occur as TPUs transition from static to dynamic mode during stretching (Fig. 5a, b). The long- and short-range structural regularities of a TPU can be examined by small- and wide-angle X-ray scattering (SAXS and WAXS) techniques, respectively. To investigate static mode, we examined undrawn samples. While **Es-MD** presents characteristic SAXS patterns arising from clear phase separation (Supplementary Figs. 16 and 17), both **C-IP-SS** and **E-IP-SS** do not exhibit distinct SAXS patterns because they are poorly phase separated. When examined by WAXS, only **Es-MD** displayed a dim peak, which is evidence for the presence of crystalline hard segments (Fig. 5a and Supplementary Fig. 18).

To investigate dynamic mode, we analyzed strained translucent specimens. **C-IP-SS** and **E-IP-SS** still failed to show any SAXS peaks, indicating that external stress does not lead to phase separation. **C-IP-SS** showed the most noticeable change in its 1D WAXS spectrum when deformed at high strain (Fig. 5b), which suggests that **C-IP-SS** undergoes a distinct structural conversion into a crystalline form. Two peaks appeared at q values of 14.0 and 16.1 nm^{-1} in the 1D WAXS spectrum when stretched to 400%; these peaks correspond to the (020) and (110) planes of crystalline methylene groups, respectively⁵⁸, with two

clear spots observed in the equatorial region of the 2D WAXS pattern (Fig. 5a). Stretched carbonate-type soft segments have relatively regular and aligned secondary structures and therefore form metastable crystals in which methylene segments are laterally packed with the aid of the ordered H-bonding array (Supplementary Fig. 19). Consequently, **C-IP-SS** stiffens and becomes as strong as commercial **Es-MD**. On the other hand, **E-IP-SS** shows a strain-independent amorphous halo 2D WAXS pattern, and 400% elongation of **Es-MD** provides a clearer spot in the equatorial region of its 2D WAXS pattern and a small change in the 1D pattern compared to that prior to stretching. The hard domain is oriented along the stretching axis with minor crystallite growth. The minor amounts of strain-induced crystallization reveals that **Es-MD** and **E-IP-SS** behave like classic elastomers that observe almost isothermal entropic elasticity (i.e. ΔH or $\Delta U \approx 0$).

The 2D pattern of the relaxed **C-IP-SS** was acquired (Supplementary Fig. 20) and reveals that its metastable crystals had fully returned to the original amorphous phase upon unloading due to the instantaneous nature of its ordered H-bonding array. Meanwhile, the strain recovery of **C-IP-SS** degraded when held for a prolonged time (72 h) at 400% strain (Fig. 5a, b), which indicates that the metastable crystal structure is stabilized upon long-term extension due to more organized lateral stacking and H-bonding.

Practical Calculation Of Reversible Mechano-responsive Crystallization

The full strain recovery of **C-IP-SS** is consistent with the phase-conversion-induced elasticity observed for biomaterials⁵⁹. The egg-capsule wall of a channeled whelk was reported to exhibit highly reversible extensibility in which internal-energy return prevails over entropic relaxation upon unloading⁶⁰. In other words, the reversible deformation of **C-IP-SS** is a non-isothermal process with an internal energy change that occurs through mechano-responsive crystallization. The internal energy contribution to the elasticity of **C-IP-SS** was evaluated on the basis of a well-established thermodynamic framework, as encapsulated by the following Eq. (1):

$$f = f_U + f_S = \left(\frac{\partial U}{\partial L}\right)_{T,V} - T \left(\frac{\partial S}{\partial L}\right)_{T,V} = \left(\frac{\partial U}{\partial L}\right)_{T,V} + T \left(\frac{\partial f}{\partial T}\right)_{L,V} \quad (1)$$

where U and S are the internal energy and entropy of the system, respectively, and L , T , and V are the length, temperature, and volume of the specimen, respectively. The total elastic force (f) is the sum of the changes in U and S as functions of L (f_U and f_S) at constant V and T ⁴⁸; f_S is determined from an f versus T term through Maxwell's relationship. Figure 5c displays tensile stress–strain graphs of **C-IP-SS** at various temperatures between -30 and 40 °C, from which f versus T plots at particular strains (i.e., L) were constructed (Fig. 5d). A classic elastomer has a positive slope because it is an isothermal system; hence $f_U = 0$ and f_S decreases with L , and $f_S < 0$, which leads to entropy-driven elasticity^{29,61}. However, the plots for **C-IP-SS** have negative slopes at all examined L and T values, which means that stretching

changes the internal energy (i.e. $f_U \neq 0$). The U term prevails over the S term for f . It is quite noticeable that the slope critically changes at 0 °C, which is close to the glass-transition temperature (T_g) (Supplementary Fig. 21). The steeper slope indicates that a higher internal-energy change results in more-stable and ordered crystals, which is associated with the following observations. **C-IP-SS** was drawn and released above its T_g ; the original strain is then recovered because of its relatively unstable crystal phases. However, **C-IP-SS** is not reversible below T_g because relatively stable crystals are formed. The energy (ΔU) required to form the stress-induced metastable crystal is calculated to $\sim 6.47 \text{ cal cm}^{-3}$ above T_g , the details of which are described in Supplementary Note 1 (Supplementary Figs. 22–24 and Supplementary Table 4). At a TPU density of 1.25 g cm^{-3} , this value can be converted into $\sim 5.17 \text{ cal g}^{-1}$. The calculated heat of the metastable crystal is 3 – 10-times lower than those ($15 - 65 \text{ cal g}^{-1}$) of stable commercial-polymer crystals⁶², which qualitatively shows that the instantly formed strain-induced crystal is unstable.

Biocompatibility Testing

The toughness, resilience, and self-repairability features of **C-IP-SS** resemble those of biological tissue. In particular, we expect that this TPU can be used as a precursor material for artificial muscle due to its high mechanical and elastic-recovery performance. Accordingly, the *in vivo* biocompatibility of **C-IP-SS** was evaluated by the Daegu Gyeongbuk Medical Innovation Foundation (DGMIF), a contract clinical research organization, following the ISO 10993-6 Annex A standard⁶³, and ethically approved by the Institutional Animal Care and Use Committee (Korea) (IACUC; approval code DGMIF-19042402-00). Experimental sample films of **C-IP-SS** (diameter: 10 mm) were implanted in the subcutaneous tissue of rats ($n = 5$), and a polyurethane film containing residual DMSO (solvent) and a high density polyethylene (HDPE) film were used as positive and negative controls, respectively (Fig. 6a). The rats were euthanized after 12 weeks and the subcutaneous tissue samples were histopathologically analyzed after routine fixing and dyeing. The histopathological tissue images reveal that **C-IP-SS** produced less inflammatory cells than the positive control (Fig. 6b). Inflammatory responses were scored semi-quantitatively by a pathologist following the ISO 10993-6 inflammatory-reaction intensity guidelines: non-irritant < slight < moderate < severe. The **C-IP-SS** film scored the lowest inflammatory intensity; i.e., non-irritant. In the preliminary experiments performed in this study, **C-IP-SS** showed superior biocompatibility and did not elicit chronic or severe inflammation.

Discussion

It is no exaggeration to state that self-healing polymers will transition toward commercialization if their mechanical performance meets industrial requirements. The uniquely designed carbonate-type macrodiol-based TPU developed in this study exhibited a tensile strength of 43 MPa, which is as high as industrially used elastomers with strong healing abilities. The key to the success of this TPU rests with its similarity to biological tissue; it operates in dual mode by responding to external stress through a

reversible structural disorder-to-order transition of its H-bonding array. In static mode, the amorphous and disordered TPU matrix facilitates rapid segmental motion that promotes reversible self-healing bond exchange. Despite this self-healing behavior, this TPU, which contains a high-density internal H-bonding structure formed through its carbonate groups, delivered twice the elastic modulus of similar materials. This carbonate-type TPU exhibited strain-induced hardening and crystallization in dynamic mode due to a transformation toward the ordered mechano-responsive H-bonded array responsible for the strong and tough properties observed in the stretched state. In addition, as evidenced by X-ray, rheology, and temperature-dependent tensile studies, the major determining factor responsible for the full recovery of the phase transition is a non-isothermal process with an associated internal energy change of 5.17 cal g^{-1} , which is smaller than that associated with a stable polymeric crystal. Furthermore, its good biocompatibility highlights its promise for use in biomedical applications. We conclude that this mechano-responsive dual mode of operation captures both mechanical and self-healing performance at commercially relevant levels.

Methods

Materials

Poly(hexamethylene carbonate) diol (HPCD, $M_n = 1,000 \text{ g mol}^{-1}$) and commercial thermoplastic polyurethane (**Es-MD**, 5575AP grade) were kindly provided by the Dongsung Corp. (Korea). Isophorone diisocyanate (98%), *N,N'*-dimethylacetamide (DMAc, 99.8%), and dibutyltin dilaurate (DBTDL, 95%) were purchased from Sigma-Aldrich (USA), and bis(4-hydroxyphenyl)disulfide (98%) was purchased from TCI (Japan) and were used without further purification.

TPU synthesis

A typical polymerization procedure has been reported by us previously⁴⁷. A typical polymerization procedure for **C-IP-SS** is described below. HPCD (C, 15.8 g, 15.8 mmol) was placed in a dried glass vessel equipped with a mechanical stirrer and heated in an oil bath at $100 \text{ }^\circ\text{C}$ under vacuum ($< 133 \text{ Pa}$) for 1 h to remove any moisture, after which it was cooled to $70 \text{ }^\circ\text{C}$. Isophorone diisocyanate (IP, 7.38 g, 33.2 mmol) and DBTDL (0.050 g, 1800 ppm) dissolved in DMAc (8 mL) were added dropwise to the reaction vessel, with stirring continued for 2 h under a N_2 atmosphere. After the pre-polymer had been synthesized, the reactor was cooled to room temperature and bis(4-hydroxyphenyl)disulfide (SS, 3.96 g, 15.8 mmol) dissolved in DMAc (15 mL) was added (as a chain extender) to the reactor. The reactor was heated to $40 \text{ }^\circ\text{C}$ and the reaction was continued until the NCO peak in the FT-IR spectrum of the mixture has disappeared, which required 1.5 h for **C-IP-SS**. For further characterization, the final concentration of the **C-IP-SS** solution was adjusted to 40 wt% by the addition of DMAc. M_w : $24,100 \text{ g mol}^{-1}$, PDI: 1.46. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): $\delta = 7.37\text{--}7.27$ (d, 4H), $6.84\text{--}6.71$ (d, 4H), $4.17\text{--}4.07$ (t, 24H), $4.07\text{--}3.97$ (br, 4H), $2.96\text{--}2.80$ (br, 4H), $1.79\text{--}1.51$ (br, 40H), $1.49\text{--}1.30$ (br, 28H), $1.12\text{--}0.71$ (br, 18H).

Film preparation, self-Healing and tensile testing

A 40 wt% DMAc solution of TPU was poured onto a Teflon sheet and gradually heated from 60 to 100 °C over 48 h. Residual solvent was removed by vacuum drying at 110 °C for 12 h. A TPU film was prepared using a hot-press machine (Ocean Science Co., COAD1007b, Korea) and pressed into Teflon molds at 130 °C and 100 bar for 5 min. The prepared films were 100 mm × 100 mm × 1 mm in size. Mechanical and self-recovery properties were examined with a universal testing machine (UTM) (Instron 5943, USA), loaded with a 1 kN load cell and driven at a constant crosshead speed of 100 mm min⁻¹ at room temperature (25 °C). A 1-mm-thick dumbbell-shaped sample (ISO 37 – 4) was cut in half with a blade, and then reattached to evaluate its self-healing properties. Temperature-dependent tensile testing at various temperatures between – 30 and 40 °C was performed using a UTM (Instron 5982, USA) equipped with a temperature-controlled chamber.

Structural characterization

¹H NMR spectroscopy was conducted on an Advance 300 MHz spectrometer (Bruker, USA). The molecular weights and molecular-weight distributions of the polymers were determined by gel permeation chromatography (GPC) using ACQUITY APC XT columns (Waters, USA) at 40 °C on an instrument equipped with a refractive index detector, with tetrahydrofuran (THF) as the mobile phase. The M_n , M_w , and polydispersity index (PDI) were calculated relative to linear polystyrene standards. Attenuated total reflection (ATR)–FT-IR spectra were acquired on a Nicolet iS50 instrument (Thermo, USA). All TPU films were scanned 32 times at a resolution of 4 cm⁻¹. The transmittance of each film was measured on a UV-2600 UV/vis spectrometer (SHIMADZU, Japan). DSC was performed on a Q-2000 instrument (TA Instruments, USA) between – 90 and 180 °C in a N₂ atmosphere at a heating/cooling rate of 10 °C min⁻¹. One-dimensional wide- and small-angle X-ray scattering profiles were obtained using synchrotron radiation ($\lambda = 1.28 \text{ \AA}$) on the 3C SAXS I beamline of the Pohang Accelerator Laboratory (PAL). The wavelength and pixel size were 1.229 and 0.079 mm, respectively. The sample to detector distance was 1.929 m for SAXS and 0.012 m for WAXS. Portable stretcher equipment was used to elongate the ~ 1-mm-thick dumbbell-shaped samples. Dynamic mechanical analysis (DMA) was performed using a Q800 instrument (TA Instruments, USA) at a fixed frequency of 1 Hz. The test specimens were bar-shaped films that were approximately 12.8 mm × 5.5 mm × 0.35 mm in size. Experiments were carried out at a heating and cooling rate of 3 °C min⁻¹ from – 80 to 80 °C in a N₂ atmosphere.

Rheology

Rheological properties were examined on an oscillatory rheometer (MCR302; Anton Paar, Austria) using a 25 mm parallel plate-plate geometry. Prior to each experiment, approximately 0.5–0.9 mm thick film samples were prepared, and each film sample was placed between the parallel plates. A temperature-sweep experiment was carried out between 25 and 95 °C at an ω and shear strain of 1 rad s⁻¹ and 1%, respectively. In addition, frequency sweeping was carried out in the 0.05 – 500 rad s⁻¹ ω range at a constant shear strain of 1%. The yield stress, which provides the minimum energy required to collapse the internal structure, was obtained from a modified Casson plot using the Eq. (2) as follows²⁰:

$$G''^{1/2} = G''_y^{1/2} + K\omega^{1/2} \quad (2)$$

in which G''_y is the yield stress and K is a constant. The segmental relaxation behavior of each TPU was examined on the basis of the relaxation time obtained from the frequency-sweep data⁶⁴:

$$J' = G' / ([\eta^*]\omega)^2 = \lambda / [\eta^*] \quad (3)$$

in which, J' is compliance, G' , η^* , and λ are the storage modulus, complex viscosity, and relaxation time, respectively. The τ_s was obtained from the λ value at 0.05 rad s^{-1} . In order to establish a time-temperature superposition (TTS) master curve, data were acquired at intervals of $10 \text{ }^\circ\text{C}$ in the $25\text{--}85 \text{ }^\circ\text{C}$ range. TTS master curves of G' and G'' for **E-IP-SS** and **C-IP-SS** were constructed from the frequency-sweep data by shifting the data to the reference temperature ($25 \text{ }^\circ\text{C}$). The frequency shift factor, α_T , was determined as follows⁶⁵:

$$\alpha_T = \frac{\omega(T)}{\omega(T_0)}$$

$$G'(T, \alpha_T\omega) = G'(T_0, \omega)$$

$$G''(T, \alpha_T\omega) = G''(T_0, \omega) \quad (4)$$

The value of α_T obtained at each temperature is summarized in Supplementary Table 5.

In vivo biocompatibility test

All surgical procedures were conducted by Daegu Gyeongbuk medical innovation foundation (DGMIF) (<http://www.dgmif.re.kr/eng/index.do>), a public contract clinical research organization, with the approval of the national institutional review board (IRB). The samples were implanted in male Sprague–Dawley rats (8-weeks-old, 250–300 g) ($n = 5$). The rats were allowed free access to food and water in room under the temperature- and humidity-controlled conditions ($22 \text{ }^\circ\text{C}$, 50%) with a 12/12 h day/night cycle (8 am/8 pm). Each rat was anesthetized using an intramuscular injection of 50 mg ml^{-1} Zoletil 50 (tiletamine and zolazepam; Virbac, Carros, France) and 23 mg ml^{-1} Rompun (xylazine; Bayer, Leverkusen, Germany), and the incision of the scalp proceeded carefully. One experimental sample (**C-IP-SS**) and one negative control (HDPE) films (10 mm diameter circle) were implanted in two different regions (15 mm

incision) of subcutaneous rat tissues. The incised skins were closed with 4/0 Dafil sutures (Ethicon, Somerville, NJ, USA) and disinfected with a povidone after whole procedures. After the surgery, the rats were maintained in their cages for 12 weeks, and then, the rats were sacrificed for histological analyses.

The tissue samples were routinely dehydrated, paraffin embedded, cut, and stained with haematoxylin and eosin (H&E). Then, the tissue cross-sections were examined for the semi-quantitative evaluation regarding International Standard (ISO 10993-6, Annex A) criteria for biological evaluation of the local effects of medical devices after implantation by a pathologist. The local effects were estimated by comparing the tissue response caused by the experimental samples (**C-IP-SS**) and the negative control. The scoring system follows the histological evaluation of the extent of the area affected. The existence, number, and distribution of polymorphonuclear cells, lymphocytes, plasma cells, macrophages, giant cells, and necrosis were evaluated. Change in the tissue caused by neovascularization, fatty infiltration, and fibrosis were evaluated as well.

Data availability The source data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Competing interests

The authors declare no competing interests.

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Author Contributions

Y.E., S.-M.K., M.L., and H.J. performed the experiments and analyzed the data. Y.E., S.-M.K., J.P., and D.X.O. prepared the figures and wrote the paper. S.Y.H., J.P., and D.X.O. conceived, designed, and directed the project. All authors have given approval to the final version of the manuscript. Y.E. and S.-M.K. equally contributed to this work.

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Figures

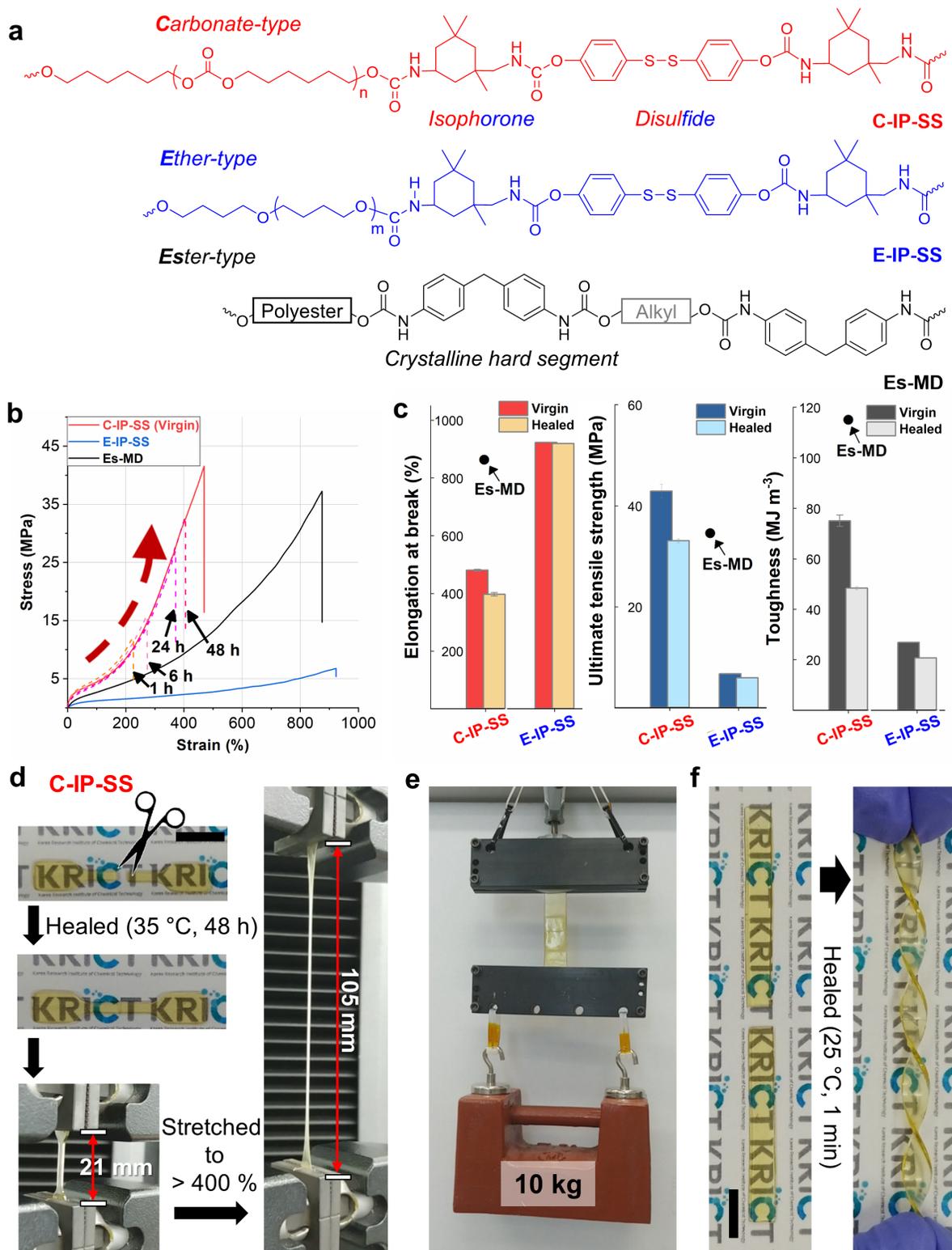


Figure 1

Chemical structures and mechanical properties of self-healable TPUs. a, Chemical structures and b, Tensile stress–strain curves for the three TPUs: C-IP-SS, E-IP-SS, and commercial Es-MD. Tensile curves of cut and rejoined C-IP-SS with different healing times at 35 °C are included. c, Comparing mechanical properties, such as elongation at break, ultimate tensile strength, and toughness, for virgin and healed TPUs. The value for the non-self-healable Es-MD is given as a point in each panel. d, Photographic

images of cut and healed C-IP-SS films before (left) and after stretching up to 400% (right) (scale bar: 1 cm). e, C-IP-SS film (thickness: 0.3 cm) cut in half, rejoined, and healed for 48 h at 35 °C, followed by a 10-kg weight-lifting demonstration. f, Photographic images of a twisted C-IP-SS film (thickness: 0.1 cm) after heating at 25 °C for 1 min (scale bar: 1 cm).

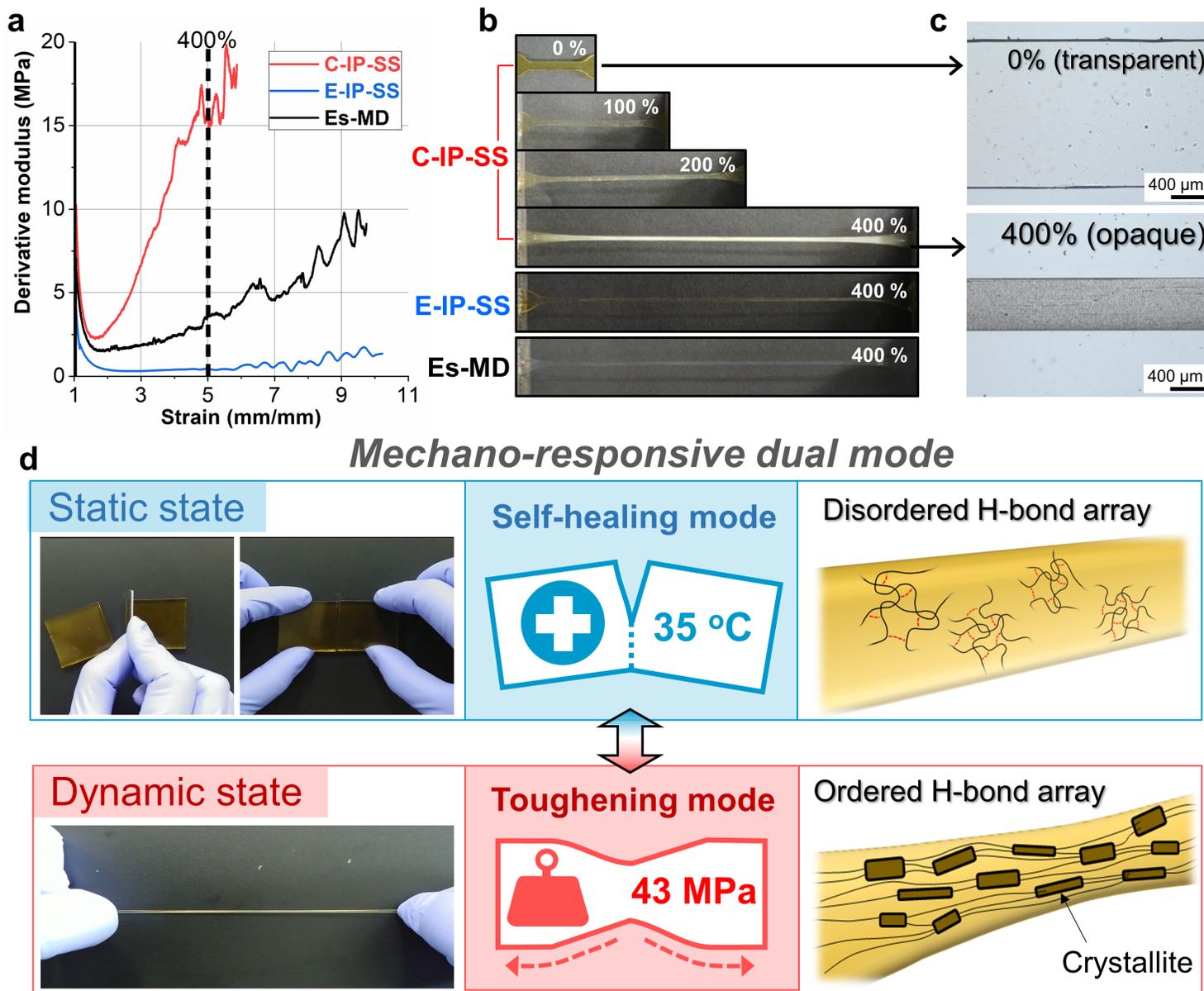


Figure 2

Mechano-responsive dual mode of C-IP-SS. a, Variations in tensile modulus versus strain obtained from the first derivatives of the tensile stress–strain curves for the TPUs (Fig. 1b). b, Macroscopic structural changes undergone by the TPUs upon uniaxial stretching to 400%. c, Optical microscopy images of unstretched and 400%-stretched C-IP-SS specimens. d, Schematic illustration of the mechano-responsive dual mode operation through the reversible disorder-to-order transition of the H-bond array: self-healing in the static state and toughening in the dynamic state.

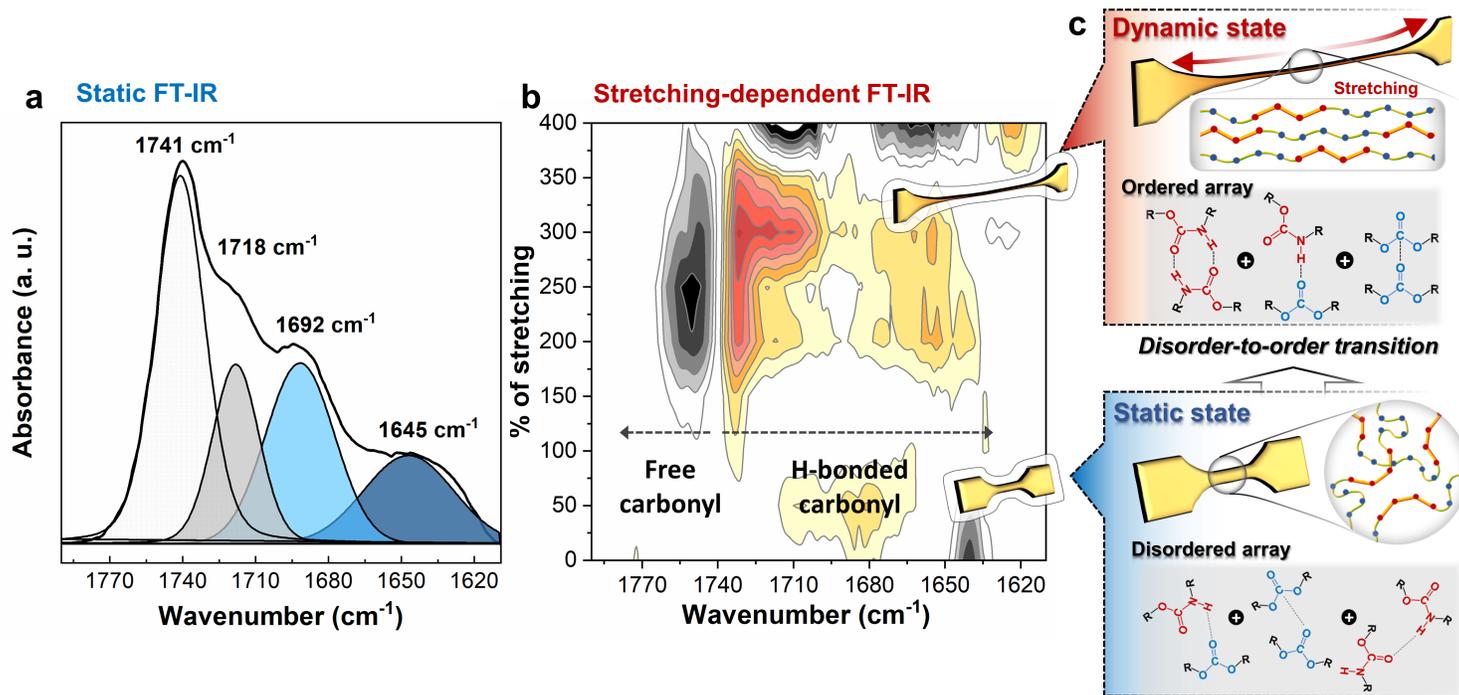


Figure 3

FT-IR analysis of C-IP-SS in the static and dynamic states. a, The carbonyl region of the FT-IR spectrum with peak deconvolution for C-IP-SS. b, 2D gradient map of FT-IR spectra with respect to stretching percentage. The red contour lines represent positive values of dA/dE , i.e., an increasing trend in absorbance as function of the degree of extension, and vice versa for the gray contour lines. c, Schematic illustration of the mechano-responsive changes in chain alignment and the associated H-bond arrays for C-IP-SS.

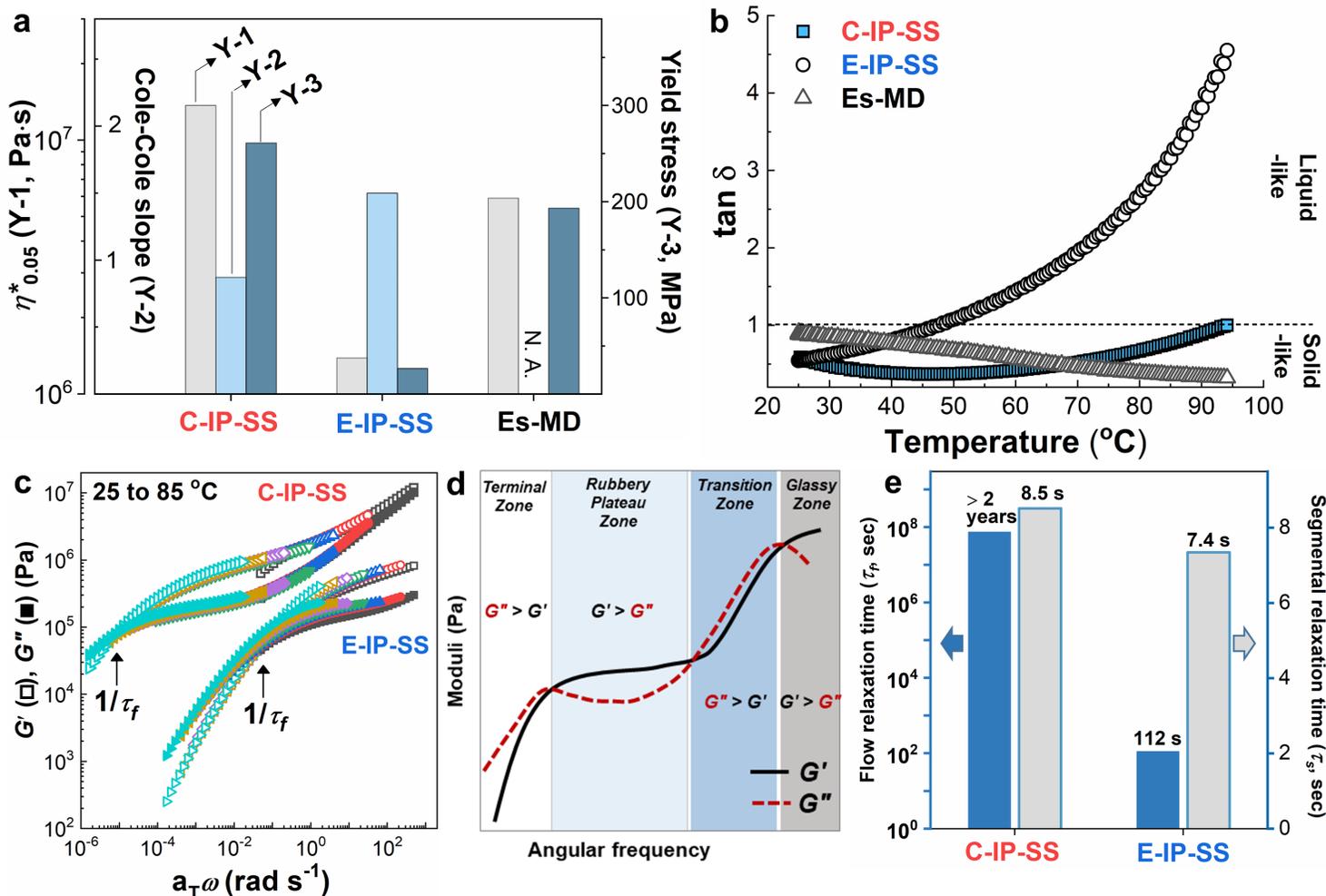


Figure 4

Rheological evidence for self-healing mechanisms. a, Rheological parameters for the three TPUs in static mode: complex viscosities ($\eta^*_{0.05}$) were obtained from viscosity curves at 0.05 rad s⁻¹ (Supplementary Fig. 13a). Yield stresses were calculated from Casson plots (Supplementary Fig. S13b) and Cole–Cole plot slopes were obtained at 25 °C (Supplementary Fig. S13c). b, Variations in loss tangent (tan δ) over the 25–95 °C temperature range at 1 rad s⁻¹. The dashed line indicates tan δ = 1. c, Master curves of storage (G') and loss (G'') moduli for C-IP-SS and E-IP-SS. The reference temperature is 25 °C. d, Illustration depicting the representative G' and G'' master curves. e, Relaxation times for chain flow transition (τ_f) and segmental motion (τ_s) for C-IP-SS and E-IP-SS at 25 °C. The τ_f values were determined from the reciprocal values of the crossover frequencies of the G' and G'' master curves (Fig. 4c), and the τ_s values were obtained from relaxation curves at 0.05 rad s⁻¹ that were calculated using equation (3) (Supplementary Fig. 14).

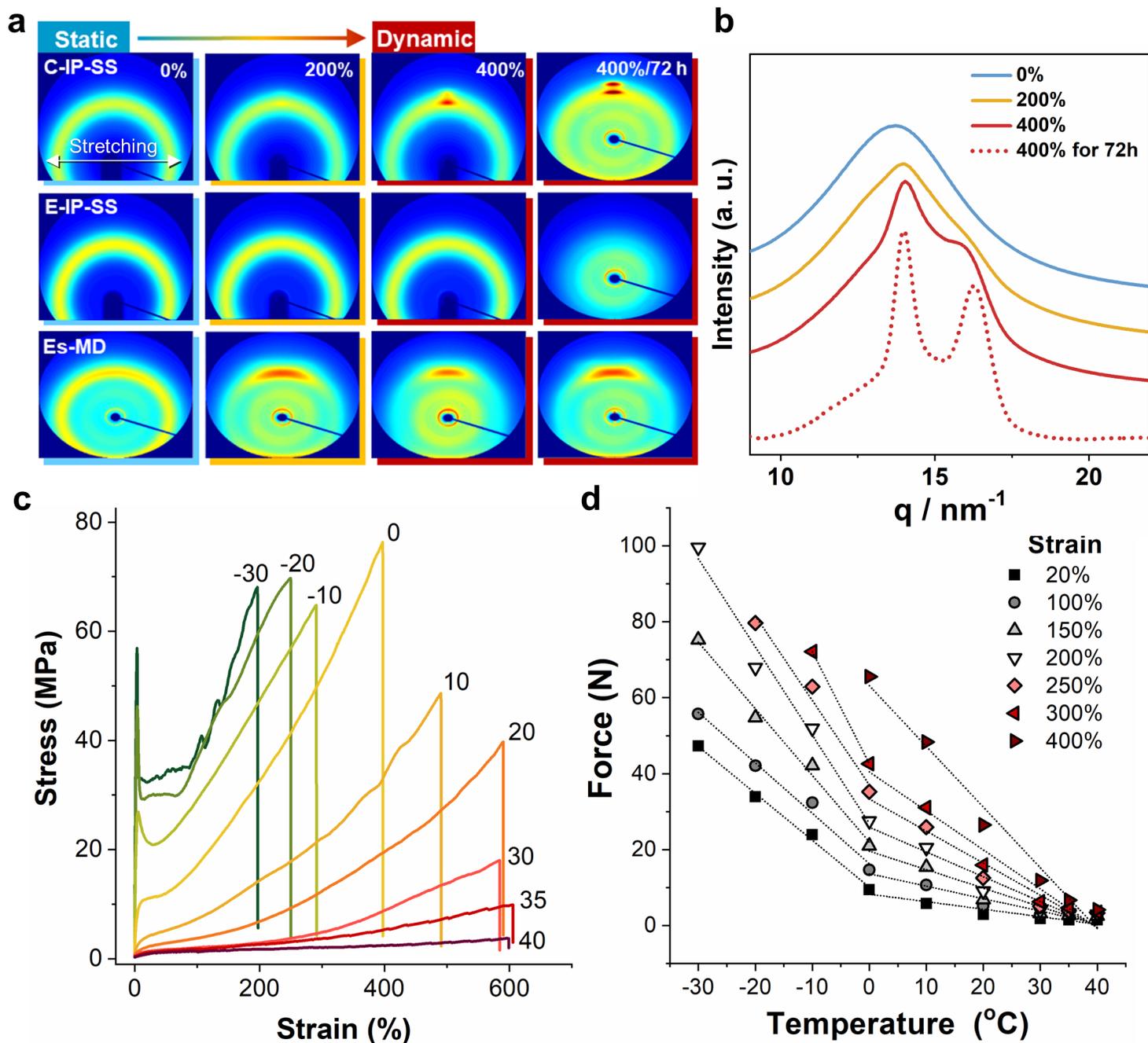


Figure 5

X-ray and thermodynamic analyses of strain-induced phase transition. a, 2D WAXS images of three TPUs at stretching ratios of 0, 200, and 400%. The WAXS results of 400%-stretched samples and that were held for 72 h are also included to trace further structural evolution. b, 1D WAXS profiles of C-IP-SS at various degrees of stretching. c, Stress–strain curves of C-IP-SS at various temperatures in the -30 to 40 $^{\circ}\text{C}$ range. d, Force versus temperature plots at various strains based on the stress–strain curves.

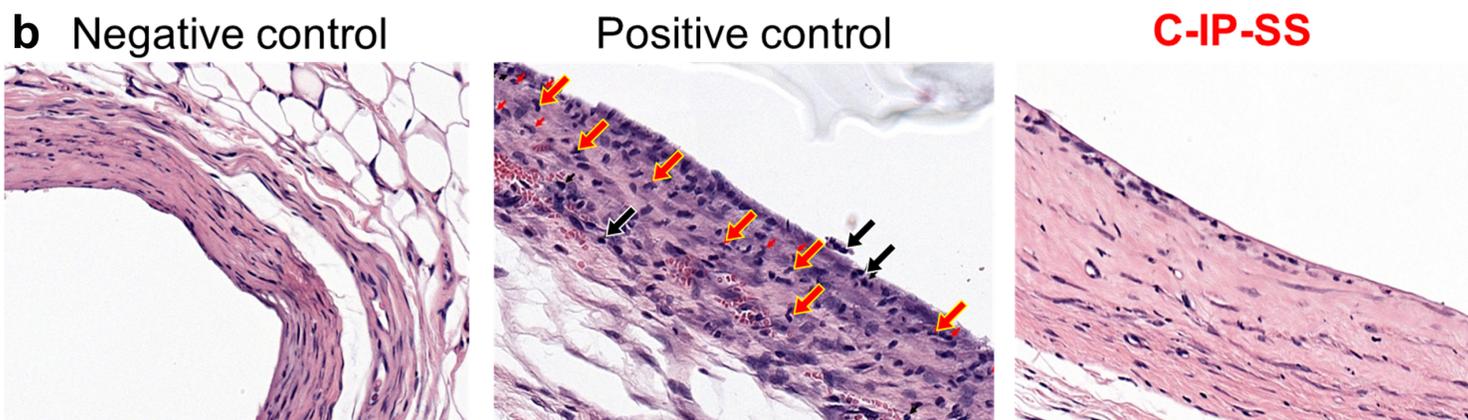
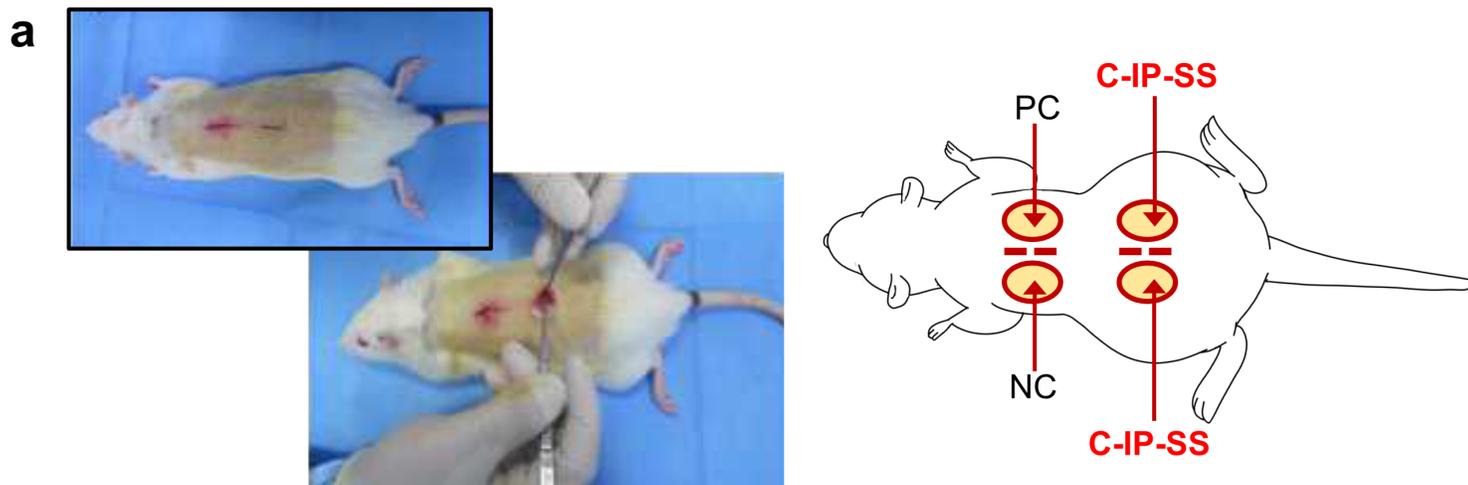


Figure 6

Biocompatibility test of C-IP-SS. a, Experimental procedure for in vivo cytotoxicity testing: rat subcutaneous connective tissues with negative control (NC, HDPE), positive control (PC, DMSO-containing polyurethane), and the C-IP-SS film. b, Representative histopathologic tissue images after 12 weeks of healing. Arrows indicate inflammatory cells (red: polymorphonuclear cells; black: lymphocytes).

Supplementary Files

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