Wireless Wearables

The cover depicts an exercising user wearing wireless, skin-interfaced electronic and microfluidic devices encapsulated with thermoplastic elastomers (TPEs). TPEs, unlike their thermoset counterparts, represent materials that are recyclable, compatible with industrial manufacturing, and low-cost, illustrating the broad applicability of these materials towards emerging wireless bioelectronic and microfluidic device technologies. More details can be found in article 2300732 by Jan-Kai Chang, Ralph G. Nuzzo, John A. Rogers, and co-workers.

ELECTROLYTES

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Thermoplastic Elastomers for Wireless, Skin-Interfaced Electronic, and Microfluidic Devices

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Wireless, skin-interfaced electronic and microfluidic devices have the potential to replace wired, bulky, and cumbersome technologies for personal and clinical health monitoring, allowing care to extend from hospital settings to the home. For use on skin, these devices commonly employ silicone-based thermoset elastomers (TSEs) as layers that encapsulate the electronics or serve as molded microchannels for biofluid (e.g., sweat) capture, storage, and analysis. Barriers to commercial adoption of such devices include difficulties in use of these elastomers in conventional practices for mass manufacturing. Their relatively high cost and inability to allow for recycling represent additional disadvantages. By contrast, thermoplastic elastomers (TPEs) are fully compatible with industrial-scale manufacturing processes, low in cost, and recyclable. Like TSEs, TPEs are soft, stretchable, flexible, and optically transparent, while possessing other properties well-suited for applications in wireless, skin-interfaced devices. Herein, the characteristics, processing, and application techniques for three commercially available TPEs, including two thermoplastic polyurethanes as encapsulation layers for a wireless skin hydration sensor and one thermoplastic styrenic block copolymer for a microfluidic sweat analysis platform, are reported. The results demonstrate that TPEs can be effectively integrated into these classes of devices, as a compelling alternative to TSEs, as a mass-manufacturable, sustainable materials option.

1. Introduction

A large collection of research and development efforts in academic labs^[1-4] and early-stage ventures^[5-7] focus on aspects of the design, development, and applications of soft, wireless, and skin-interfaced devices-both electronic and microfluidic-as cost-effective, userfriendly technologies for comprehensive personal health monitoring.^[8–10] To afford soft, skin-compatible mechanical characteristics, such devices commonly employ low modulus thermoset elastomers (TSEs), either as encapsulation structures for electronic physiological monitors or as microfluidic networks for sweat sensors.^[3,8,11-13] The broad commercial availability of medical-grade TSEs make these materials attractive in small-scale fabrication for exploratory research and/or for initial commercialization activities. The thermoset nature of TSEs represents, however, a barrier to adoption for mass production, as these materials are incompatible with

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J. L. Ciatti, J. Berkovich, J. A. Rogers Department of Materials Science and Engineering Northwestern University Evanston, IL 60208, USA J. B. Model, R. Ghaffari Epicore Biosystems, Inc. Cambridge, MA 02139, USA A. Banks, J.-K. Chang Wearifi Inc. Evanston, IL 60208, USA industrial-scale manufacturing.^[14–16] Comparatively high materials costs and more importantly, the inability to be recycled/remolded.^[17-18] represent additional disadvantages. Thermoplastic elastomers (TPEs) are an alternative class of soft, stretchable materials that avoid these drawbacks.^[15-17,19-23] Certain TPEs offer many of the most desirable characteristics of TSEs and other types of vulcanized rubbers (e.g., mechanically soft and compliant, stretchable, and flexible at ambient conditions), with the reprocessability of thermoplastic polymers. These comparatively low-cost materials (typically an order of magnitude less than their TSE counterparts) are compatible with common industrial-scale manufacturing practices, such as injection molding, extrusion processing, stereolithography, blow molding, compression molding, and thermoforming; they also enable remolding/recycling.^[15-16,19-21] TPEs are thus promising material candidates for sustainable and high-volume use with wireless, skin-interfaced electronic and microfluidic devices.

According to ISO-18064 standards, TPEs can be broadly classified into six general categories and associated nomenclature: 1) thermoplastic polyurethanes (TPU), 2) thermoplastic styrenic block copolymers (TPS), 3) thermoplastic polyamides (TPA), 4) thermoplastic copolyesters (TPC), 5) thermoplastic vulcanizates (TPV), and 6) thermoplastic polyolefins (TPO).^[24–25] These diverse chemistries, and corresponding wide range of mechanical properties, provide a vast materials library, enabling users to select properties that match requirements for desired applications.

Here, we present the characterization and processing of three commercially available TPEs for two different classes of skininterfaced devices: 1) polyether- and polyester-based TPUs^[26–29] as encapsulation materials for wireless, skin-interfaced electronic devices, with demonstrations in a recently developed skin hydration sensor (SHS), and a 2) styrene-ethylene/butylenestyrene (SEBS)-based TPS^[15–16,19–21] as a material for microfluidic structures, with demonstrations in a sweat sensor de-

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signed to measure sweat loss, sweat rate, and sweat chloride concentration ([Cl-]). Comparisons benchmark these TPE materials against the most widely used, commercially available silicone-based TSEs (e.g., Silbione (Silbione RTV 4420, Elkem), poly(dimethylsiloxane) (PDMS) (Sylgard 184, Dow Corning)). The results suggest superior characteristics in mechanical strength and stretchability, bonding strength, and adhesion to medical-grade skin adhesives, with reduced water vapor transmission rates for sweat storage. Thermoforming and hot embossing of these TPE materials yield patterned layouts for these functional devices, while reinforcing mesh structures can further enhance the physical toughness and integrated thermochromic leuco dyes can provide colorimetric indicators for thermal safety. Human subject trials illustrate levels of performance comparable to those possible with standard TSEs. The collective results suggest promising routes to sustainable, widespread use of TPEs in skin-interfaced devices.

2. Results and Discussion

2.1. Thermoplastic Elastomers (TPEs) for the Encapsulation and Fabrication of Wireless, Skin-Interfaced Devices

The process flow (**Figure 1A**) for use of TPEs in wireless, skin-interfaced devices starts with pellets, films, and/or rolls of material, typically available at comparatively low costs ($<\approx$ \$100 kg⁻¹).^[15] Applied pressure at elevated temperatures enables thermoforming into desired layouts to serve either as encapsulation layers for electronic devices for health monitoring or as microfluidic channels for sweat analysis. After the expected device lifetime has elapsed, whether in clinical, home, fitness, or industrial environments, the encapsulation materials can be recycled and reused, as the basis for a greener, more sustainable alternative to TSEs.

Reacting diisocyanates (hard segments) with polyether/polyester-based diols (soft segments) results in TPUs, linear block copolymers with alternating hard and soft segments.^[30-32] In TPSs, which are linear ABA-triblock copolymers, a central butadiene-based block (soft segments) connects two styrenic end blocks (hard segments).^[22,23,33] Thermodynamic instability between the hard and soft segments of these various block copolymers leads to phase separation into hard and soft microdomains. At ambient conditions, which reside below the glass transition (T_{o}) and melting temperatures of the hard domain but above the T_g of the soft domain, the hard, glassy domain (also serving as physical crosslinks) provides mechanical strength and structural integrity, while the soft, rubbery domain enables stretchability and mechanical compliance. Above the recommended service temperature of the material, the physical crosslinks provided by the hard domains disappear, allowing for thermal processability, as with conventional thermoplastic polymers.

Figure 1B illustrates the general chemical structures of the two TPUs and one TPS examined in this study, highlighting the various soft and hard segments of these materials. Specifically, the polyether-based TPU (Zytar Z1A1, Biomer Technology LTD) and polyester-based TPU (Elastollan 35A, BASF) consist of alternating polyether/polyester-based soft segments and diiso-cyanate hard segments. These TPUs can serve effectively as soft

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Figure 1. Thermoplastic elastomers (TPEs) for the encapsulation and fabrication of wireless, skin-interfaced devices. A) Schematic diagram illustrating the process flow for TPEs used in encapsulation of wireless, skin-interfaced devices. B) General chemical structures of the commercial TPEs investigated in this work, including polyether/polyester-based thermoplastic polyurethanes (TPUs) and styrene-ethylene/butylene-styrene (SEBS), a thermoplastic styrenic block copolymer (TPS).

encapsulation structures for wireless, skin-interfaced electronic devices, as demonstrated subsequently. For skin-interfaced sweat microfluidic device fabrication, a SEBS-based TPS (FlexdymTM, Eden Tech), comprising a hydrogenated ethylene/butylene soft midblock with styrenic hard end blocks, satisfies key requirements. The resulting electronic and microfluidic devices demonstrate performance characteristics comparable to those formed using silicone-based TSEs, with additional relevant features and benefits.

2.2. Properties of Thermoplastic Polyurethanes (TPUs) for the Encapsulation of Wireless, Skin-Interfaced Electronic Devices

The soft, robust encapsulation of wireless, skin-interfaced electronic devices serves multiple purposes, from protecting the skin against mechanical or electrical hazards associated with the internal electronics to enabling seamless, comfortable interfaces to the body.^[34] **Figure 2** presents results from the characterization of relevant properties of the two TPUs studied here, designated as "Z1A1" and "Elastollan" for the polyether- and polyester-based TPUs (Figure S1, Supporting Information), respectively. Compared to the silicone-based TSEs (Silbione RTV 4420, Elkem), designated as "Silbione", most commonly used in skin-interfaced devices, Z1A1 and Elastollan exhibit superior mechanical strength and stretchability, respectively. The stress/strain results (Figure 2A) from uniaxial stretching of these three materials indicate that Z1A1, with an ultimate tensile strength of 27.7 MPa, is \approx 575% stronger than Silbione. Although Elastollan has a lower tensile strength (≈ 2.0 MPa), it surpasses Silbione in terms of stretchability, reaching a total elongation at break of 893%. Extraction of Young's moduli (E) from the linear elastic regions of these curves reveals that Elastollan (E \approx 2.4 MPa) is comparable in stiffness to Silbione (E \approx 1.7 MPa), whereas Z1A1 (E \approx 9.2 MPa) is stiffer. Hysteresis loops of Z1A1 and Elastollan (Figure 2B,C, respectively) illustrate mechanical hysteresis at strain levels above 20%, motivating the use of a patterned serpentine nylon mesh embedded within the TPU (Figure 2D-F), as a strain-limiting and mechanical-reinforcing mechanism.[34-35] Photographs of a piece of optically transparent (Figure S2, Supporting Information) Elastollan embedded with a patterned serpentine nylon mesh (Figure 2D) while undergoing uniaxial strain

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Figure 2. Characterization of thermoplastic polyurethane (TPU) properties for the encapsulation of wireless, skin-interfaced electronic devices. A) Stress/strain curves of two commercial TPUs, a polyether-based TPU (Z1A1) and a polyester-based TPU (Elastollan), and that of a medical-grade thermoset silicone elastomer (Silbione). B) Hysteresis loops of the Z1A1 TPU. C) Hysteresis loops of the Elastollan TPU. D) Photographs of a patterned serpentine nylon mesh integrated within the Elastollan TPU. E) Photographs illustrating the Elastollan TPU/patterned serpentine nylon mesh composite undergoing uniaxial strain. F) Stress/strain profiles of Elastollan TPU and the Elastollan TPU/patterned serpentine nylon mesh composite, highlighting the difference in modulus between the two materials at \approx 25% strain. G) Photographs illustrating the color changes of Elastollan TPU integrated with a thermochromic leuco dye upon heating at 50 °C.

(Figure 2E) show that the triangular layout of the serpentine pattern causes an increase in stiffness above strains of $\approx 20\%$ (Figure 2F). For example, at a strain of 25%, the modulus of Elastollan (E ≈ 0.95 MPa) increases by 174% to 2.6 MPa with the embedded nylon mesh. As in previous work, this nonlinear, strainadaptive stiffening behavior can be adjusted through selection of various geometrical parameters of the mesh (e.g., serpentine angle, serpentine width) to meet application requirements.^[34–35]

Typical power sources (e.g., lithium polymer batteries, coin cells) for such devices pose potential safety risks to users, as thermal runaway associated with battery failures may yield temperatures that surpass the pain and damage thresholds (48 °C) for human skin.^[34,36] In this context, thermochromism in the encapsulation layers can serve as a beneficial and protective safety mechanism, allowing for visually observable signs of an overheating device to prompt quick removal from the skin. Recent work demonstrates that thermochromic leuco dyes with activation temperatures of 47 °C can be incorporated into a self-healing dynamic covalent elastomer to provide such safety warnings.^[34]

This concept can be used with Elastollan by incorporating this leuco dye as an additive within the TPU matrix, via solution casting (Figure 2G). Heating this thermochromic Elastollan TPU composite (3 wt% dye, thickness $\approx 600 \ \mu$ m) on a hot plate (50 °C) reveals a uniform and dramatic color change from dark magenta to a light shade of pink after ≈ 30 s. This feature can be used in tandem with other mechanisms (e.g., thermally actuated liquid-vapor bladders for thermal isolation, evaporative cooling, protection circuits/thermal switches, embedded hollow glass microspheres) to improve the thermal safety of wireless, skin-interfaced devices.^[34,36–38]

2.3. Hybrid Thermoplastic Polyurethane (TPU) Encapsulation of a Wireless Skin Hydration Sensor (SHS)

As Figure 2A demonstrates, of the two TPUs, Z1A1 possesses higher mechanical strength, whereas Elastollan is significantly more elastic and softer. These different properties form the

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Figure 3. Hybrid thermoplastic polyurethane (TPU) encapsulation of a wireless, skin-interfaced electronic device designed to measure skin hydration. A) Schematic representation of the thermoforming process to fabricate the polyester-based TPU (Elastollan) top layer. B) Schematic representation of the hybrid encapsulation structure of the skin hydration sensor (SHS), comprising two different TPUs-the polyester-based TPU (Elastollan) and the polyether-based TPU (Z1A1). C) Photographs of the encapsulated skin hydration device. D) Peel strength of the Z1A1 TPU and of a medical-grade thermoset silicone elastomer (Silbione) against silicone/acrylic-based medical adhesives. E) Sensitivity characterization of the SHS with a Z1A1 bottom layer vs. one with a fabric-reinforced Silbione bottom layer. F) Skin hydration and conductance levels of different body sites, as measured by the SHS.

basis of a hybrid encapsulation structure for a wireless SHS, where thermoforming at 149 °C (below the thermal degradation temperatures of the TPUs (Figure S3, Supporting Information)) with custom-machined aluminum molds yields an Elastollan top layer (thickness \approx 400 µm), to which a thin (thickness \approx 10 µm) patterned Z1A1 bottom layer is bonded (Figure 3A,B). Previous work on SHS devices shows that the thickness of the bottom encapsulation layer affects the sensitivity of the measurements, which rely on the transient plane source technique.^[39–41] As such, previous encapsulating structures for these devices typically employ thin (e.g., thicknesses \approx 45–120 µm) silicone bottom layers (e.g., Silbione: Ecoflex OO-30/Ecoflex Gel, Smooth-On) with embedded fiberglass fabrics (thickness $\approx 30 \,\mu$ m) for improved physical toughness.^[39-41] Since Z1A1 is significantly stronger than Silbione, the thickness of the bottom layer can be appreciably reduced, leading to thinner, lighter device profiles without the need for fabric reinforcement. The result is an enhancement in mechanical flexibility and in interfaces to the skin. Figure 3C presents photographs of a flexible and fully encapsulated SHS, featuring a purple Elastollan top layer and a thin Z1A1 bottom layer, both optically transparent to facilitate viewing of the internal electronic circuitry.

Application of wireless, skin-interfaced electronic devices to the skin often involves the use of a commercially available, medical-grade dual-sided adhesive, typically based on silicone and/or acrylic chemistries.[34,36,39-44] For robust adherence onto the skin, strong bonding must occur between the bottom encapsulation layer of the device and the adhesive. Figure 3D shows results of measurements of adhesion strength from 90° peel testing of both Z1A1 and Silbione, against each side of a dual-sided silicone/acrylic medical adhesive tape (2477P, 3M). The peak peel strengths of Z1A1 against the silicone- and acrylic-based sides of the adhesive tape are ≈0.5 and ≈1.1 N cm⁻¹, respectively. Dramatically lower in comparison to Z1A1, the peak peel strengths of Silbione against the same silicone- and acrylic-based sides of the adhesive tape are ≈0.3 and ≈0.1 N cm⁻¹. Z1A1 significantly outperforms Silbione in adhesion to both silicone- and acrylicbased medical-grade adhesives. For the acrylic-based adhesive, the strength of the Z1A1 interface surpasses that of Silbione by more than an order of magnitude.

Measurements with SHSs formed using Z1A1 and fabricreinforced Silbione bottom layers indicate similar performance in sensitivity (Figure 3E) and in extracted skin hydration levels (Figure 3F) at various body locations. Moreover, compared to high-frequency conductance measurements from a skin surface hygrometer (SKICON-200EX-USB, Yayoi Co.),^[45–46] the SHS captures the same trends in skin hydration across the body. As expected, the forehead exhibits the highest average values of skin hydration (~80%) and conductance (≈108 µS). These results demonstrate the applicability of TPU-encapsulated SHSs in monitoring trends in skin hydration, with implications for dermatological healthcare.

2.4. Properties of Thermoplastic Styrenic Block Copolymer (TPS) for the Fabrication of Wireless, Skin-Interfaced Sweat Microfluidic Devices

Vinvl-terminated PDMS TSEs (Sylgard 184, Dow Corning) are traditionally preferred materials for soft microfluidic devices. The optical transparency and capacity for surface modifications of this material, together with its ability to replicate fine features in lithographically defined master molds, enable the fabrication of 3D channel networks for capture and manipulation of microliter fluid volumes.[47-49] The high material costs (>\$100 kg⁻¹) and the nonrecyclable nature of PDMS represent some disadvantages.^[14-17] Others include the diffusion of oligomeric content from the bulk of the polymer, incompatibility with various organic solvents, extensive steps in processing (e.g., mixing, degassing, thermal curing, oxygen (O2) plasma treatment, and bonding), and relatively high water vapor permeability (Table S1, Supporting Information).^[50,51] In this context, TPEs are promising alternatives. Indeed, recent work illustrates the use of a commercial, soft, and biocompatible SEBS-based TPS, hereby designated as "Flexdym", as a low-cost (as low as \$10 kg⁻¹ of raw pellets), rapidly processable, and optically transparent material for various microfluidic device applications, such as cell culture on-chip environments for bioassays, passive perfusion assays, capillary pumps, and acoustic micromixers.^[19-21,52] Here, we extend the use of this material for our intended applicationskin-interfaced sweat microfluidic devices. Figure 4 summarizes measurements of various properties of Flexdym relevant to the fabrication and use of such devices.

Surface modification and hydrophilization of Flexdym are essential requirements for fabricating microfluidic structures. O₂ ADVANCED MATERIALS TECHNOLOGIES www.advmattechnol.de

plasma treatment of Flexdym for different times results in decreases in static water contact angle (WCA) (Figure 4A; Figure S4A. Supporting Information) to levels below 90°, indicating hydrophilicity. A treatment time of 30 s results in the lowest static WCA of ≈63°. Figure 4B summarizes static WCA measurements of pristine Flexdym and Flexdym after 30 s of O₂ plasma treatment, including samples subsequently subject to various aging conditions, for room temperature/ambient conditions over two weeks (Figure S4B, Supporting Information) and for thermal incubation at 75 °C over 1 day. Hydrophobic recovery—relevant and advantageous for sweat rate measurements^[53-55]—occurs when O2 plasma-treated Flexdym is subject to these aforementioned aging conditions. The thermally aged, O₂ plasma-treated Flexdym reaches a WCA of 96°, the same value as pristine Flexdym. Moreover, O₂ plasma treatment and thermal incubation significantly affect the bonding and adhesion between layers of Flexdym. The peak peel strength between two O₂ plasma-treated and thermally incubated Flexdym layers reaches ≈ 13 N cm⁻¹, or $\approx 13 \times$ larger than that between two unmodified Flexdym layers (Figure 4C).

The results of mechanical characterization of Flexdym appear in Figure 4D,E. The TPS material is soft (E \approx 2.0 MPa) and elastic (elongation at break \approx 710%) (Figure 4D), with mechanical hysteresis at strains above 20% (Figure 4E). The material also displays high optical transparency (Figure 4F), greater than 70% from wavelengths ranging from 300 to 800 nm. These mechanical and optical characteristics of Flexdym are similar to those of PDMS.

Flexdym outperforms PDMS, however, with respect to sweat absorption (Figure 4G) and water vapor permeability (Figure 4H; Table S1, Supporting Information), two metrics that are important for sweat microfluidic devices, specifically in storage of sweat without loss into the materials or the surrounding environment. Specifically, sweat absorption measurements of PDMS reach peak values of $\approx 0.6\%$ after 1 h, while those of Flexdym are only $\approx 0.2\%$ after 2 h. As in Figure 4H, Flexdym exhibits a water vapor transmission rate (WVTR) of ≈ 36 g m⁻² d⁻¹, which is $\approx 11\times$ lower than that of PDMS^[50–51] (Table S1, Supporting Information). These results suggest that Flexdym, with lower sweat absorption and WVTR, compared to PDMS, is the more optimal material for sweat analysis, as it can help to contain and confine all captured sweat within the channels, without evaporative or absorption losses that may contribute to inaccurate measurements.

2.5. Thermoplastic Styrenic Block Copolymer (TPS) Fabrication of a Wireless Sweat Microfluidic Device

A schematic representation of the skin-interfaced sweat microfluidic device^[7,55] structure studied here appears in **Figure 5**A. The device comprises a Flexdym layer (thickness \approx 0.95 mm) with molded microfluidic channels and reservoirs for inlets and colorimetric assays. Patterning of this layer occurs via a hot embossing procedure (Figure 5B), where applied heat (180 °C) and force (\approx 11 N) for 30 min in vacuum against a silicon master mold yields channels with depths of \approx 330 µm. Scanning electron microscope images illustrate representative molded channel and reservoir structures (Figure 5C) of the device, as fabricated from the hot embossing procedure. Other related microfluidic device features, such as capillary burst valves (Figure S5, Supporting

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Figure 4. Characterization of thermoplastic styrenic block copolymer (TPS) properties required for the fabrication of wireless, skin-interfaced sweat microfluidic devices. A) Representative water contact angle photographs of the styrene-ethylene/butylene-styrene (SEBS) TPS (Flexdym) as a function of O₂ plasma treatment times. B) Contact angle measurements of the Flexdym TPS, including after exposure to O₂ plasma treatment (30s) and other various aging conditions (e.g., room temperature (RT) for 2 weeks, incubation at 75 °C for 1 d). C) Peel strength measurements of two O₂ plasma-treated/thermally aged (75 °C for 1 d) Flexdym TPS films and of two pristine Flexdym TPS films. D) Stress/strain curve of the Flexdym TPS. E) Hysteresis loops of the Flexdym TPS. F) UV–vis transmittance spectrum of the Flexdym TPS. G) Sweat absorption measurements of the Flexdym TPS and thermoset poly(dimethylsiloxane) (PDMS), incubated at 37 °C. H) Water vapor transmission properties of the Flexdym TPS.

Information), are also possible. O₂ plasma treatment of this patterned channel layer and a thin capping Flexdym layer (thickness ≈ 0.25 mm) and subsequent bonding seals the channels, forming microfluidic networks. Use with a medical-grade, double-sided skin adhesive with a white background (Microfluidic Diagnostic Tape 9965, 3M) prepares the device for bonding on the skin and subsequent visualization for colorimetric analysis. After device use is complete, the medical-grade skin adhesive can be removed and disposed, allowing for eventual reuse/recycling of the TPE materials.

Sweat chloride concentration ([Cl⁻]) is a valuable parameter to monitor, in both clinical health and personal fitness contexts.^[7,10,53–58] The former is relevant as elevated [Cl⁻] levels in sweat represent the standard method for cystic fibrosis diagnosis,^[56–57] whereas the latter can aid in the optimization of hydration and electrolyte replenishment for elite performance athletes.^[7,55,58–59] Indeed, [Cl⁻] can be identified via visual colorimetric readout, as the reaction between a silver chloranilate reagent and [Cl⁻] in sweat yields a chloranilate acid ion with tones of purple that depend on concentration (Figure 5D).^[17,55,56] The

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Figure 5. Thermoplastic styrenic block copolymer (TPS) fabrication of a wireless, skin-interfaced sweat microfluidic device designed to measure chloride levels in sweat. A) Schematic representation of a sweat microfluidic device fabricated from the styrene-ethylene/butylene-styrene (Flexdym) TPS. B) Schematic representation of the processing steps required for the fabrication and assembly of sweat microfluidic devices using the Flexdym TPS. C) Scanning electron microscopy images of various molded structures (e.g., channels, reservoirs) in the Flexdym TPS microfluidic sweat device. D) Standard calibration curve (Chroma (C*)) obtained from image processing to determine chloride concentration ([Cl⁻]) values, along with the corresponding exponential model fit. E) Photographs of the Flexdym TPS sweat microfluidic device worn on the left forearm of a 27-year-old female subject in a cycling session. F) Colorimetric analysis of chloride concentration ([Cl⁻]) in sweat obtained from the same subject in (E) wearing the Flexdym TPS sweat microfluidic device after undergoing a 45-min cycling session.

color intensity of the reacted sweat in the microchannels is proportional to [Cl⁻]; higher [Cl⁻] shows up as darker purple hues and vice-versa. Chroma (C^{*}) is a commonly used parameter in video and image processing systems to quantitatively describe the color signal of an image.^[55,56] Here, image processing reveals that low [Cl⁻] concentrations (\approx 20 mM) result in an average chroma (C^{*}) value of \approx 6 a.u., while high [Cl⁻] concentrations (\approx 100 mM) appear as a more vibrant shade of purple (C^{*} \approx 13 a.u.); the relationship can be described by an exponential fit.

[CI-] (mM)

By incorporating the silver chloranilate reagent in the reservoir immediately adjacent to the inlet of the device, captured sweat reacts with the reagent to produce a color change in the following microchannels. Demonstration of the Flexdym sweat microfluidic device appears in Figure 5E, where a volunteer subject, undergoing a vigorous cycling session, wears the device on left forearm, without any observable device delamination from the skin. After 45 mins, sweat enters and fills part of the device, reacting with the reagent and producing a light shade of purple in the resultant microchannels.

Subsequent analysis reveals that $[\rm Cl^-]$ is ${\approx}20$ mM after the cycling session.

3. Conclusion

TPEs are a promising class of soft polymer materials that provide simple routes for sustainable encapsulation and fabrication of wireless, skin-interfaced electronic and microfluidic devices. The collective results presented here illustrate the feasibility and applicability of two commercial TPUs (e.g., Z1A1 and Elastollan) for a hybrid encapsulation structure of a wireless sensor that tracks meaningful trends in the hydration state of skin, and one commercial TPS (e.g., Flexdym) for fabrication of a wireless microfluidic device that measures [Cl⁻] in sweat. These materials can readily apply to other related skin-interfaced devices, with potential for integration with industrial-scale manufacturing processes as a route to widespread adoption of these types of technologies.

4. Experimental Section

TPE Materials: Pellets of a polyether-based TPU (Zytar Z1A1 80 A, Biomer Technology LTD) and of a polyester-based TPU (Elastollan EXP B CF 35 A 12 P TSG, BASF) were dried in air at 90 °C for 4 h before processing. Films of varying thicknesses (0.25-2.0 mm) of a SEBS TPS (Flexdym, Eden Tech) were used as received.

Patterning of Strain-Limiting and Mechanically Reinforcing Nylon Meshes: General design principles and mechanical characteristics of patterned serpentine mesh networks can be found elsewhere.^[34–35] Nylon-6 films (#142-214-93, Goodfellow Corporation; thickness \approx 250 µm) were patterned with a laser cutter (Protolaser R, LPKF).

Integration of Patterned Serpentine Nylon Mesh with Elastollan TPU: A solution of Elastollan in tetrahydrofuran (THF) was poured into a Teflon dish (diameter: 60 mm) and solvent removal at 60 °C yielded an Elastollan film (thickness \approx 0.6 mm). Placement of the patterned nylon mesh^[34] on top of this film, followed by a complete covering of the mesh with additional Elastollan solution and solvent removal at 60 °C yielded an Elastollan/patterned nylon mesh composite material (thickness \approx 1.5 mm).

Integration of Thermochromic Leuco Dye with Elastollan TPU: 3 wt% thermochromic leuco dye (LCR Hallcrest), with an activation temperature of 47 °C, was added to a solution of Elastollan in THF, with the aid of 20 min sonication. Then, the mixture was poured into a Teflon dish. Removing the solvent at 60 °C overnight yielded a thermochromic Elastollan composite material (thickness $\approx 600 \,\mu$ m).

Encapsulation of a Wireless Skin Hydration Sensor (SHS): Elastollan or Z1A1 pellets were dissolved in THF by stirring on a hot plate at room temperature overnight. Casting Elastollan solution containing \approx 15 g Elastollan into a glass petri dish (diameter: 140 mm) followed by removing the solvent at 60 °C overnight yielded an Elastollan film with a thickness of \approx 800 um. Thermoforming this Elastollan film, using custom-machined convex and concave aluminum molds, at 149 °C for 15 min, generated an Elastollan top layer with a thickness of ${\approx}400~\mu\text{m}.$ The 8 wt% Z1A1 solution was applied to the surface of a glass microscope slide with two parallel, 200µm-thick strips of polyimide tape as spacers, and a glass microscope slide was used as a squeegee to remove any excess. The \approx 10 μ m-thick Z1A1 bottom layer was formed after the solvent was removed at 60 °C for 5 min. The wireless SHS flexible printed circuit board was bonded to the Z1A1 bottom layer, via a thin layer of Z1A1 solution. Subsequent bonding of the top Elastollan and bottom Z1A1 layers, via a thin layer of Z1A1 solution, yielded a fully encapsulated device.

SHS Device Characterization and Hydration Measurements: Details regarding the sensitivity characterization of the SHS with Z1A1 or fabricreinforced Silbione bottom layers can be found elsewhere.^[39–41] All experiments involving human participants were carried out upon the approval of the protocol (STU00209010) of the Northwestern University Institutional Review Board and informed written consent was obtained from the participants. Application of the SHS to the precleaned skin of varying body locations of a 35-year-old male subject was performed. The hydration level of the skin was determined with the SHS, while the skin conductance was determined with a skin surface hygrometer^[45–46] (SKICON-200EX-USB, Yayoi Co.). The presented results are the average and standard deviation of three measurements per body location.

Fourier Transform Infrared (FTIR) Spectroscopy: Solid state FTIR transmission spectra of TPU materials (e.g., Z1A1, Elastollan) were obtained with a Thermo Scientific Nicolet iS50, over a range of 4000 to 400 cm⁻¹. FTIR of Z1A1 (cm⁻¹): v = 3325 (m; v(N-H)), 2852 (s; v(C-H)), 1701 (s; v(C = O)). FTIR of Elastollan (cm⁻¹): v = 3330 (w; v(N-H)), 2956 (m; v(C-H)), 1728 (s; v(C = O)).

UV–vis Spectroscopy: Solid-state UV–vis transmission spectra of TPE materials were obtained with a Perkin Elmer LAMBDA 1050 spectrophotometer, over a range from 200 to 800 nm.

Mechanical Characterization: Stress/strain profiles of TPE materials were obtained from uniaxial tensile tests (strain rate = 0.1 mm s^{-1}) with a dynamic mechanical analyzer (RSA-G2 Solids Analyzer, TA Instruments).

Peel Strength Measurements: Polyimide tape was bonded to the thin films of Z1A1 or Silbione (Silbione RTV 4420, Elkem), and a thin film of polylactic acid was bonded to the thin films of Flexdym. These served as backing layers to minimize the contribution of elastic energy dissipation to the test results. A dynamic mechanical analyzer (RSA-G2 Solids Analyzer, TA Instruments) was used for 90° peel tests of samples with a width of 1 cm, at a peel speed of 60 mm min⁻¹.

Fabrication of Flexdym TPS Microfluidic Channels: Flexdym TPS films (thickness ≈ 1.2 mm) were cut to shape and placed on top of a 4-inch, lithographically defined silicon master mold containing previously reported device designs.^[7,55] Hot embossing consisted of placement of an aluminum block (≈ 1.1 kg) on top of the Flexdym film and heating for 30 min at 180 °C in a vacuum oven, yielding patterned TPS films (thickness ≈ 0.95 mm).

Assembly of Sweat Microfluidic Device: The colorimetric assay solution was made by dispersing 50 mg of silver chloranilate (Green Room Board Co.) in 200 μ L of 2 wt.% polyhydroxyethylmethacrylate methanolic solution. Five microliters of the mixture was drop casted into the reservoir designed for chloride sensing. After the assay was dried, the Flexdym TPE channel (thickness \approx 0.95 mm) and capping layers were exposed to oxygen plasma for 30 s (20 sccm, 10 Pa, 100 W). Adhering the Flexdym TPE channel layer and capping layer together and incubating the microfluidic device in an oven at 75 °C for one day completed the bonding process. Adhering a layer of white, double-sided medical-grade adhesive tape (Microfluidic Diagnostic Tape 9965, 3M) to the bottom of the microfluidic device yielded a ready-to-use device.

Water Contact Angle Measurements: A contact angle goniometer (VCA Optima XE, AST Products) was used for static contact angle measurements of deionized (DI) water. 0.2 µL droplets of DI water were used for each measurement. The presented results are the average and standard deviation of 4 contact angle measurements taken per sample.

Sweat Absorption Characterization: Samples of Flexdym and PDMS (Sylgard 184, Dow Corning) were immersed in artificial sweat and incubated at 37 °C. The change in weight of the sample with time was measured. The presented results are the average and standard deviation of three samples.

Water Vapor Permeability Characterization: The water vapor permeability of Flexdym was characterized according to ASTM E96 protocols. Briefly, a 20 mL glass scintillation vial was filled with a desiccant (Drierite, W.A. Hammond Drierite Company), and a 250-µm-thick film of Flexdym sealed the opening of the vial. The vial was placed into closed chamber containing an open petri dish filled with water. The weight of the filled vial was measured over a period of 10 days, yielding the water vapor transmission rate (WVTR). The presented results are the average and standard deviation of 3 vials.

Chloride Concentration ([Cl-]) Colorimetric Analysis: The calibration curve was determined from raw images, obtained from a DSLR camera (Canon 90D), of standard samples corresponding to the physiologically relevant levels of chloride (20, 40, 60, 80, 100 mm), with a 24-color card

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for color correction. Images were processed using a Python script extracting CIELAB color values (*L**, *a**, and *b**) for calculation of chroma (C*), according to the equation: $C^* = (a^{*2}+b^{*2})^{1/2}$. The presented results are the average and standard deviation of 4 separate areas of the captured images.

Scanning Electron Microscopy (SEM): Molded Flexdym TPS samples were first coated with 18 nm of osmium by a Filgen Osmium Plasma Coater. The surface morphologies of these conductive samples were then characterized with a Hitachi SU-8030 SEM, with an acceleration voltage of 5.0 kV and a working distance of 12.5 mm.

Sweat Microfluidic Device Application and Testing: All experiments involving human participants were carried out upon the approval of the protocol (STU00207078) of the Northwestern University Institutional Review Board and informed written consent was obtained from the participants. A fully assembled Flexdym sweat microfluidic device was placed and adhered onto the precleaned, left ventral forearm of a 27-year-old female subject. The subject exercised for 45 min on a stationary bicycle. After the exercise trial was completed, photographs of the sweat-filled device were taken with a DSLR camera (Canon 90D) and subsequently analyzed to extract the [Cl⁻] concentration.

Supporting Information

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

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Conflict of Interest

One of the authors (JAR) is co-founder of early stage companies (Wearifi and Epicore Biosystems) that are pursuing commercialization of devices related to those reported here.

Data Availability Statement

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

Keywords

encapsulation, sustainability, sweat microfluidics, thermoplastic elastomers, wireless wearables

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