AFRL-RX-WP-JA-2020-0186

A LOW-COST, COMPOSITE COLLAGEN-PDMS MATERIAL FOR EXTENDED FLUID RETENTION IN THE SKIN-INTERFACED MICROFLUIDIC DEVICES (POSTPRINT)

Benjamin Heo, Michael Fiola, Ji Hyun Yang and Ahyeon Koh

State University of New York at Binghamton

27 July 2020
Interim Report

AIR FORCE RESEARCH LABORATORY
MATERIALS AND MANUFACTURING DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
27 July 2020	Interim	18 September 2018 – 27 June 2020

4. TITLE AND SUBTITLE
A Low-cost, Composite Collagen-PDMS Material for Extended Fluid Retention in the Skin-interfaced Microfluidic Devices
(Postprint)

5a. CONTRACT NUMBER
FA8650-18-2-5402

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
62102F

6. AUTHOR(S)
Benjamin Heo, Michael Fiola, Ji Hyun Yang and Ahyeon Koh - State University of New York at Binghamton
(Continued on next page)

5d. PROJECT NUMBER
4348

5e. TASK NUMBER

5f. WORK UNIT NUMBER
X1EM

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
AFRL/RX
2977 Hobson Way (Continued on next page)
Wright-Patterson AFB OH 45433

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory
Materials and Manufacturing Directorate
Wright-Patterson Air Force Base, OH 45433-7750
Air Force Materiel Command
United States Air Force

10. SPONSORING/MONITORING AGENCY ACRONYM(S)
AFRL/RXAS

11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)
AFRL-RX-WP-JA-2020-0186

12. DISTRIBUTION/AVAILABILITY STATEMENT
DISTRIBUTION STATEMENT A. Approved for public release: distribution is unlimited.

13. SUPPLEMENTARY NOTES
PA Case Number: 88ABW-2020-2402; Clearance Date: 27 Jul 2020. This document contains color. Journal article published in Colloid and Interface Science Communications, Vol. 38, online 11 Aug 2020. © 2020 Elsevier B.V. The U.S. Government is joint author of the work and has the right to use, modify, reproduce, release, perform, display, or disclose the work.
The final publication is available at https://doi.org/10.1016/j.colcom.2020.100301

14. ABSTRACT *(Maximum 200 words)*
The advancement of soft, wearable microfluidic devices relies on the microfabrication of polydimethylsiloxane (PDMS) using soft lithography techniques. However, thin 3D microstructures made of PDMS limit long-term storage of aqueous samples and reduce the accuracy of onboard sensing modalities within the platform because of the material's high permeation of water vapor. We studied a composite material of collagen microparticles and PDMS that greatly reduces water evaporation while maintaining the properties of a soft elastomer required for skin-interfaced microfluidics. The collagen-PDMS material is biocompatible, affordable, and non-toxic. We reduced permeability by 80.2% by building a film containing 30 wt% collagen microparticles. Mechanical properties, such as elastic modulus and bonding efficacy, can vary as a function of particle concentration in the films. The skin-interfaced collagen-PDMS microfluidic devices increase sweat retention by 45% through 9 h compared with pure PDMS. This material can greatly improve the long-term sample storage of epidermal devices.

15. SUBJECT TERMS
Collagen microparticle, PDMS composite, water permeability, Sweat collection

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT:	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON (Monitor)
a. REPORT	b. ABSTRACT	c. THIS PAGE			Jeremy Ward
Unclassified	Unclassified	Unclassified	SAR	9	19b. TELEPHONE NUMBER *(Include Area Code)* (937) 255-9717

REPORT DOCUMENTATION PAGE Cont'd

6. AUTHOR(S)

Benjamin Heo, Michael Fiola, Ji Hyun Yang and Ahyeon Koh - State University of New York at Binghamton

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Biomedical Engineering
State University of New York at Binghamton
4400 Vestal Pkwy E
Binghamton NY 13902

Colloid and Interface Science Communications 38 (2020) 100301

Contents lists available at ScienceDirect

Colloid and Interface Science Communications

journal homepage: www.elsevier.com/locate/colcom

Rapid Communication

A low-cost, composite collagen-PDMS material for extended fluid retention in the skin-interfaced microfluidic devices

Benjamin Heo[1], Michael Fiola[1], Ji Hyun Yang, Ahyeon Koh*

Department of Biomedical Engineering, State University of New York at Binghamton, Binghamton, NY, USA

ARTICLE INFO

Keywords:
Collagen microparticle
PDMS composite
Water permeability
Sweat collection

ABSTRACT

The advancement of soft, wearable microfluidic devices relies on the microfabrication of polydimethylsiloxane (PDMS) using soft lithography techniques. However, thin 3D microstructures made of PDMS limit long-term storage of aqueous samples and reduce the accuracy of onboard sensing modalities within the platform because of the material's high permeation of water vapor. We studied a composite material of collagen microparticles and PDMS that greatly reduces water evaporation while maintaining the properties of a soft elastomer required for skin-interfaced microfluidics. The collagen-PDMS material is biocompatible, affordable, and non-toxic. We reduced permeability by 80.2% by building a film containing 30 wt% collagen microparticles. Mechanical properties, such as elastic modulus and bonding efficacy, can vary as a function of particle concentration in the films. The skin-interfaced collagen-PDMS microfluidic devices increase sweat retention by 45% through 9 h compared with pure PDMS. This material can greatly improve the long-term sample storage of epidermal devices.

1. Main text

Recent advances in skin-interfaced sweat sensing systems provide in situ physiological and biochemical information, such as sweat rate and chloride concentration in sweat [1–4]. Significantly increased attention to sweat analysis has accelerated the development of epifluidics, the skin-interfaced microfluidic devices capable of conformally contacting with the skin while harvesting the sweat for bioanalysis [5–9]. The epifluidic devices are realized using thin, 3D microstructures made of elastomeric materials, typically polydimethylsiloxane (PDMS), that are capable of direct collection and storage of sweat by using advanced structural design and system integration [1–4] [10],. However, PDMS has high vapor permeability that limits the storage time of sweat in thin epifluidics that are kept at body temperature [11]. A biofluid sample stored in a thin PDMS microfluidic device begins evaporating during sample collection, which results in inaccurate measurements of biomarker concentration [12]. Thus, it is crucial for the collected samples to be tested upon close time frame of collection by onboard sensing modalities. Otherwise, sample analysis becomes increasingly difficult due to transportation over long distances for laboratory instrumentations [9]. Studies of composite materials have sought to alter the properties of PDMS through the use of additives. For example, graphene [13], silica nanoparticles [14], and silver [15] have been used to create PDMS composites with altered conductivity, mechanical strength, and antimicrobial properties, respectively, while maintaining other properties of PDMS [12]. Skin is itself a waterproof composite material comprised of many different proteins, including collagen. We hypothesize that a collagen PDMS composite which mimics human skin could be less permeable to water vapor. Additionally, collagen has demonstrated the ability to reduce water vapor permeability of PDMS with a focus on application in a micro-total analysis system (μTAS) [16]. Collagen plays a critical role in the interactions between cells and the extracellular matrix in the human body [17], and it has been used in drug delivery [18], tissue engineering [17], and wound healing applications [19]. Collagen is not only biocompatible but exhibits high water absorption properties that allow it to serve as a barrier to water transmission through a bulk material [20]. These properties make collagen a promising material to be investigated for use in PDMS composites that could be integrated into epidermal microfluidic devices. While pure collagen is available for research applications, it is also available cheaply as a dietary supplement. In this study, we investigate the collagen-PDMS composite embedded with low-cost nutraceutical fish collagen microparticles. The collagen-PDMS composite significantly reduces the evaporation of water vapor, thus extending biofluid storage time. The composite material also maintains favorable mechanical properties, such as an elastic modulus similar to the

* Corresponding author.
E-mail address: akoh@binghamton.edu (A. Koh).
[1] Both authors contributed equally to this manuscript.

https://doi.org/10.1016/j.colcom.2020.100301
Received 4 May 2020; Received in revised form 15 July 2020; Accepted 16 July 2020
Available online 11 August 2020

epidermis and bonding efficacy that allows for the fabrication of multilayered microfluidic devices while still enabling the use of soft lithography. Additionally, the skin-interfaced collagen-PDMS microfluidic devices were fabricated with a 3D printing system to demonstrate low-cost sweat collection and storage patch-type microfluidic devices that can retain fluid for a long time.

The PDMS composites materials were prepared and tested for water vapor permeability using low cost ($0.26/g) and commercially available fish collagen (Rousselot, WI). Collagen particles were ground with a mortar and pestle followed by water-bath sonication that resulted in decreased particle size and improved homogeneous dispersion. Particles untreated in this matter resulted in films containing an uneven collagen distribution (Fig. S1). The microparticles of collagen were dispersed in uncured PDMS which was then prepared in films. This process created a PDMS dominant interface allowing for further engineering (e.g., soft lithography) (Fig. S1). In addition to collagen, other known skin biocompatible materials such as silicone rubber thickener Ure-Fil 9 (Smooth-On; PA), and zeolite (Sigma-Aldrich; MO) were used as additives for direct comparison against collagen-PDMS composite (Fig. S3).

Collagen-PDMS films were incorporated in epidermal sweat collectors via soft lithography and improve biosample retention despite evaporation being driven by body heat from skin interface (Fig. 1A). Sweat collection devices were fabricated using soft lithography techniques and a stereolithography 3D printing system to allow for an economically affordable manufacturing process. Devices present a thickness of 2 mm and a diameter of 3 cm. Although our device is thicker than the devices previously reported (thickness of 700 μm), the fabricated device functions in mechanical adaptability on the skin and efficient sweat collection [8]. Sweat collectors consisted of multiple layers containing channels, an indicator dye, and adhesive (Fig. 1B). The addition of collagen particles to PDMS decreases the optical transparency of the material resulting in an elastomeric, opaque white film (Fig. 1C). Particles covered 46 ± 5% of film area imaged using an optical microscope. The treated particles each occupied an average area of 31.28 ± 3.45 μm^2 (~3 μm radius particles) when embedded within the film (Fig. 1D). Reduced optical transparency did not affect visualization of the collected sample within the device because of the indicator dye (Fig. 1E–F). Natural pressure from sweat glands introduces sweat into the epidermal microfluidics, which forces the indicator dye to travel through microchannels and thus visually presents a collection of sweat in real-time. With fabricated collagen-PDMS epifluidics, the sweat rate was observed ~43 $\mu L\ hr^{-1}\ cm^{-2}$ which is consistent with previously reported sweat rate values [8]. The water retention of a collagen-PDMS collection device was compared to that of a plain PDMS device. Devices were filled with water and left to sit at ambient conditions for 9 h. The collagen-PDMS epifluidics demonstrate ~45% enhanced sweat sample retention within the time period compared to the device made of pure PDMS. The increased amount of collagen in the collagen/PDMS collectors showed a corresponding decrease in the sample loss. The 30 wt% collagen-PDMS epifluidics results in 93 ± 2% sample retention after 9 h while 59 ± 8% of the sample evaporated when using pure PDMS epifluidics (Fig. 1G). This demonstrates that the interaction of collagen and PDMS particles in the composite improves

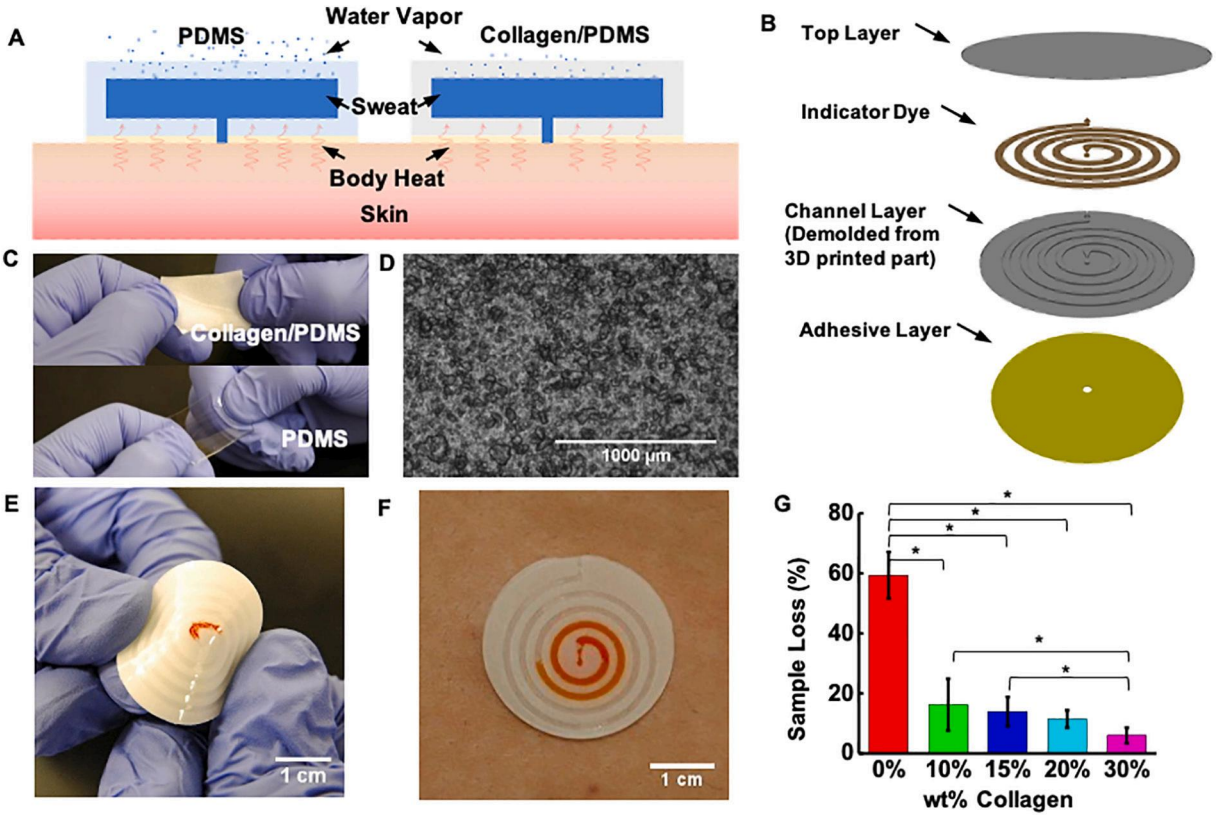

Fig. 1. Schematic diagram and morphology of collagen/PDMS composite microfluidics (A) The schematic diagram shows a comparison between a PDMS and collagen/PDMS skin-interfaced biofluid collection device. Water vapor evaporation driven by body heat is reduced when using collagen/PDMS. (B) Exploded view showing layers of the sweat collection device, including cover layer, indicator dye, channel layer, and adhesive. The top and channel layers are composed of collagen/PDMS composite. (C) Optical images of PDMS and collagen/PDMS, highlighting the deformable and stretchable properties of PDMS maintained in collagen/PDMS. (D) Optical image showing the surface of a 10 wt% collagen/PDMS film. Darker sections indicate areas of opaque collagen aggregates. (E) Optical image of deformable collagen/PDMS sweat collector, showing indicator dye before sweat collection. Thickness of the device is 2 mm. (F) Collection of sweat from the skin after 40 min of exercise. The travel of orange dye reflects of total amount of sweat collected. (12 $\mu L\ hr^{-1}$). (G) Water loss from sweat collectors after 9 h of wearing on the forearm, ($n = 3$, error bars represent standard deviation, $^*p < .05$).

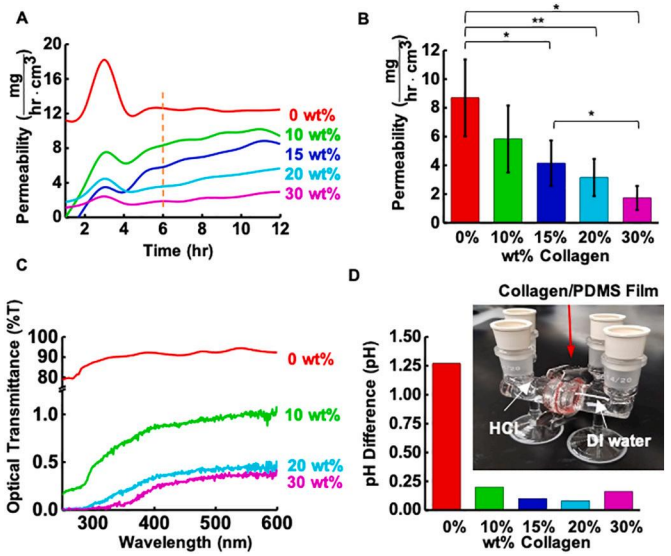

Fig. 2. Permeability of collagen/PDMS to water vapor and hydrogen ions (A) Water vapor permeability over time. Permeability fluctuates during initial hours of testing and values stabilize after 6 h. (B) Mean permeability of each sample after 6 h of testing exhibiting a decrease in water vapor permeability as additional collagen is added ($n = 4$, error bars represent standard deviation, $^*p < .05$). (C) The optical transmittance of collagen/PDMS films, highlighting the sharp increase in opacity as collagen is added. (D) Difference in pH measured after 72 h, using collagen/PDMS interface as a barrier between DI water and 0.1 M HCl. The permeability to hydrogen ions decreases as a function of collagen concentration in the film. Inset shows the H-cell apparatus used to test hydrogen ion permeability.

the fluid retention ability of collagen-PDMS epifluidic device.

Water vapor permeability of the collagen-PDMS composite films were further characterized as a function of the weight contents of collagen microparticles. Films were created using 0 wt%, 10 wt%, 15 wt%, 20 wt%, and 30 wt% collagen concentrations. Higher concentrations of collagen microparticles failed to be cast in homogenous films. Water vapor permeability was determined using Eq. (1), where the mass of water loss (Δm) divided by the hours of testing (t), surface area (A), and thickness of the film (h) and the unit of WVP presents as mg hr^{-1} cm^{-3}.

$$WVP = m/(t \times A \times h) \quad (1)$$

After the start of measurements, water vapor transmission rate through the film increased gradually until reaching an equilibrium value, which may have been caused by the saturation of water vapor within the device (Fig. 2A). However, this phenomenon was less severe as collagen particle concentration increased in the PDMS structures. Water vapor permeability decreases as collagen particle concentrations increase in PDMS films. While the average permeability value for a pure PDMS film was 8.70 ± 2.68 mg hr^{-1} cm^{-3}, a WVP of 30 wt% collagen-PDMS showed 1.72 ± 0.84 mg hr^{-1} cm^{-3} which represents an 80.2% reduction by the addition of collagen microparticles to the polymeric matrix (Fig. 2B). This demonstrates that sample loss in the collagen-PDMS devices was improved by the reduced permeation of water through collagen/PDMS structure matrix. The reduced permeation of water through the collagen/PDMS matrix may have been caused by the water sorption by collagen particles within the PDMS matrix. The cross-sectional surface SEM images of films submerged in water for 24 h shows swelling of collagen particles when compared to collagen/PDMS film at ambient conditions (Fig. S5). However, collagen/PDMS would not be exposed to similar conditions during use in epifluidics.

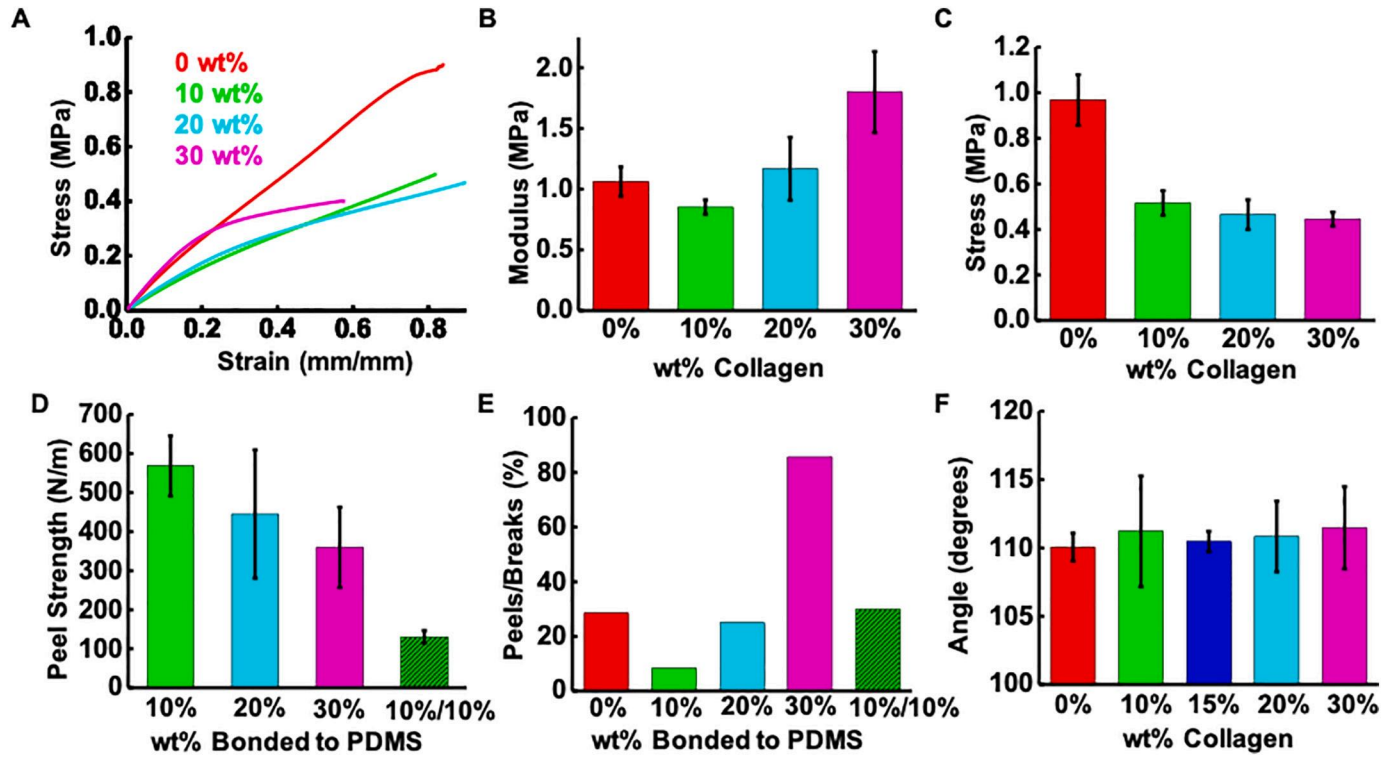

Fig. 3. Mechanical and physical characteristics of collagen/PDMS films. (A) Representative stress strain curves of different collagen/PDMS samples. Note the increase in plastic deformation as the wt% of collagen is increased. (B) Elastic modulus for collagen/PDMS samples indicating an increase in stiffness as additional collagen is added (n = 4, error bars represent standard deviation, $^*p < .05$). (C) Ultimate tensile strength (UTS) for collagen/PDMS samples, showing a decrease in UTS as collagen wt% increases in the flims (n = 4, error bars represent standard deviation, $^*p < .05$). (D) The peel strength of different wt% collagen/PDMS samples oxygen plasma bonded to PDMS (n = 3, error bars represent standard deviation, $^*p < .05$). (E) Ratio of peels/breaks when testing collagen/PDMS peel strength (collagen/PDMS is bound to PDMS except for 10%/10% sample, where collagen/PDMS was bound to collagen/PDMS). (F) Contact angle measurements of different wt% collagen/PDMS films (n = 3, error bars represent standard deviation). t-test indicates no statistically significant difference between results ($p > .49$).

Table 1
Mechanical characteristics of collagen/PDMS films. Results obtained from standard tensile and contact angle tests of various wt% collagen-PDMS films. Values indicate changes in the composite's properties as a function of collagen particle concentrtaion.

wt% collagen	Ultimate strength [MPa]	Modulus [MPa]	Failure strain [mm/mm]	Contact angle [°]
0%	0.97 ± 0.11	1.06 ± 0.12	0.87 ± 0.10	110.1 ± 1.02
10%	0.52 ± 0.05	0.85 ± 0.06	0.83 ± 0.09	111.2 ± 4.06
20%	0.47 ± 0.07	1.17 ± 0.26	0.81 ± 0.10	110.8 ± 2.58
30%	0.45 ± 0.03	1.80 ± 0.33	0.77 ± 0.17	111.5 ± 3.00

Optical transmittance tests were conducted to quantify the previously noted increase in film opacity due to microparticle addition (Fig. 2C). The PDMS microfluidic devices with multiple reservoirs and channels are susceptible to cross-contamination because of the permeability of PDMS to small molecules [8]. This is important in the case of drug delivery devices where small molecule absorption impedes efficient delivery [21]. To understand the small molecule permeability of collagen-PDMS composites, the proton permeability of the collagen-PDMS composite films was studied using an electrochemical H-cell apparatus and assessing passive diffusion of protons across the film (Fig. 2D). The pH change of a reservoir following the testing period signified the proton transmission across each film concentration. The pH changed by 1.20 ± 0.13 after 72 h with pure PDMS films. However, the collagen-PDMS films resulted in a reduction of 0.18 ± 0.02 pH and 0.05 ± 0.04 for 10 wt% and > 15 wt% films, respectively (thickness of films averaged ~570 μm). This demonstrates that a collagen particle-PDMS structure can potentially minimize the cross-contamination of different fluids (Fig. 2D).

Various mechanical properties of collagen-PDMS films were characterized. As collagen-PDMS composites are intended for use in skin-interfaced wearable microfluidics, it is important to understand how the device performs under mechanical distortions with soft and curvilinear skin. Representative stress-strain curves for collagen-PDMS composites were created following tensile testing (Fig. 3A). The failure strain of the composite was slightly reduced as more collagen was added to PDMS. Failure strain of PDMS was 0.87 ± 0.10 mm/mm. For collagen-PDMS, failure strains were 0.83 ± 0.09, 0.81 ± 0.10, and 0.77 ± 0.17 for 10, 20, and 30 wt%, respectively. The 10% collagen-PDMS films exhibited the lowest elastic modulus at 0.85 ± 0.06 MPa (Fig. 3B). The collagen/PDMS composite films had moduli comparable to the reported modulus of the epidermis (~1 MPa) [22]. The 30 wt% collagen-PDMS composite had a modulus of 1.80 ± 0.33 MPa which differed the most from the epidermis modulus as compared to other concentrations. The addition of collagen microparticles reduces the mechanical strength of the polymer. The ultimate tensile strength of pure PDMS films was 0.97 MPa, while 30 wt% collagen/PDMS films show an ultimate tensile strength of 0.45 MPa representing a 53.6% reduction. The initial addition of collagen reduces strength more significantly than further addition (Fig. 3C). For a composite material, the interactions at the interface of the additive and the bulk material play a critical role in determining the mechanical properties. High levels of adhesion at the interface allows the transfer of stress between the additive and the bulk material [23,24]. This may explain why the lower wt% composites maintain properties close to PDMS, and the 30 wt% composite has an elevated modulus. SEM analysis reveals gaps between collagen and PDMS, illustrating the poor adhesion between the materials (Fig. S2). Nevertheless, collagen-PDMS composites maintained the elastomeric properties of PDMS (low modulus and high failure strain) that are suitable for soft bioelectronics applications. Plastic deformation of the material increased with increasing collagen concentration because the presence of collagen microparticles increases the rigidity of PDMS, resulting in a stiffer material [23]. Bonding efficacy of the collagen-PDMS composite materials was tested using a T-peel test for soft lithography. One advantage of PDMS is its ability to create multilayer microfluidic devices by utilizing oxygen plasma treatment. Results show that peel strength is inversely proportional to collagen particle concentration (Fig. 3D). The 10 wt% collagen-PDMS bonding with bare PDMS had the greatest peel strength of 568 ± 77 N m^{-1}, while 30 wt % collagen-PDMS exhibits peel strength of 360 ± 103 N m^{-1}. Additionally, the bonding of two 10 wt% collagen-PDMS films together resulted in a strength of 130 ± 16 N m^{-1} (Fig. 3E). Hydrophobic surfaces have been demonstrated to decrease the pressure required for laminar flow within microfluidic devices [25]. The contact angles of the composites exhibit a range of 110.1°–111.5° showing a slight increase of hydrophobicity because of the rough surface but no significant change across varying collagen concentrations ($p > .49$) (Fig. 3F). The reported range of the contact angle for PDMS is 95°–114°, which agrees with the result found in prior studies, but the increased water retention ability in the collagen-PDMS device may be because of improved water adsorption at the surface of collagen-PDMS rather than within the bulk of the material (Table 1) [26–28].

In conclusion, collagen-PDMS composites exhibit lower water vapor permeability as compared with PDMS films. Proton permeability of PDMS was also significantly lowered in composites. Additionally, collagen-PDMS displayed moduli consistent with that of human epidermis, and hydrophobicity of the polymeric matrix is unaffected by the additive. The collagen-PDMS epifluidics significantly increase sweat sample retention over a nine-hour period. The sweat collection rate of composite epifluidics matched that of previously constructed, skin-interfaced PDMS sweat sensors. The collagen-PDMS epifluidic can be engineered with analytical modalities such as colorimetric analysis for detecting sweat rate and volume as well as physiochemical analysis. Indeed, collagen-PDMS can serve as a useful material for fabricating epidermal microfluidics for various sweat monitoring applications as well as long-term storage and transport vehicle. Future studies should elucidate the mechanism of water vapor permeability reduction. The study of the interactions at the interface of collagen and water vapor under various temperature and humidity conditions is underway. Further research in this area is underway to incorporate various natural materials and structures to improve sweat sample retention while advancing the conformability of the epifluidics.

2. Experimental section

2.1. Preparation of collagen-doped PDMS film

Collagen-PDMS composites were made using low cost ($0.26/g), commercially available, type 1 collagen. Peptan Fish Collagen (Rousselot; WI) was ground for 5 min using a mortar and pestle and was added to Sylgard 184 PDMS (Dow Corning; MI). Uncured PDMS was mixed by hand using a 10:1 ratio of base to curing agent (10:1 base:cure ratio). Collagen was added in appropriate amounts to create films of each wt%. The uncured collagen-PDMS solution was poured into 50 mL centrifuge tubes to be sonicated for 5 min using an ultrasonic cleaner (MTI Corporation; CA). After sonication, solutions were poured onto 150 mm Petri dishes to create films followed by 1 h degassing under vacuum and oven curing at 60 °C for 2 h. The size of collagen particles was measured by an optical microscope and SEM performing image analysis using ImageJ software.

2.2. Fabrication of sweat collector and sweat retention test

The spiral model for sweat collectors was designed in AutoCAD, adapting the design from a standard sweat collection system (i.e., Macroduct®), and then 3D printed using Formlabs Form 2 stereolithography printer (Formlabs; Massachusetts) using Formlabs Grey Resin. The skin-interfaced sweat collecting systems were prepared using soft lithography described in previously published papers [8,29].

Completed sweat collectors were attached to the surface of the skin using double-sided medical adhesive (3M 1524). The collagen-PDMS sweat collection devices were tested for sweat collection and water retention capabilities of the wearable microfluidics. Skin-interfaced collagen-PDMS microfluidics were placed on the lower back of the subject and collected sweat while the subject ran for 40 min on a treadmill. The sweat volume collected in the device was tracked by imaging every 10 min and further image analysis of indicator dye in ImageJ. To evaluate aqueous water retention, the mass changes of the device were monitored at ambient conditions for 9 h.

2.3. Water vapor and proton permeability testing

Permeability testing was conducted using Payne Permeability Cups (TQC Sheen; MI) following ASTM D1653 [30]. Each cup was filled with 8 g of DI water. The collagen-PDMS films were clamped between the retaining ring and the body of the permeability cup so that the film separates the water from the external environment. Cups were kept in an acrylic desiccator containing Drierite desiccant (W.A. Hammond Drierite Co.; OH) to control humidity. Temperature and humidity were maintained at 23.4 ± 0.3 °C and 37.7 ± 4.8% relative humidity, respectively. Water loss from the permeability cups was measured by weighing each cup hourly for 12 h. Permeability was calculated as the mass of water loss (Δm) divided by the hours of testing (t), surface area (A), and thickness of the film (h) (Eq. (1)).

An H-cell electrochemical apparatus was used to evaluate proton permeability with passive diffusion. Proton diffusion across the collagen-PDMS films was measured by testing the pH using a pH meter (HANNA Instruments; RI).

2.4. Mechanical testing and physical properties

Tensile testing was conducted to evaluate the physical properties of collagen-PDMS samples. For each wt% composite, two batches were prepared. Each batch provided two samples for testing resulting in four samples total per wt%. Aluminum molds yield dog bone-shaped samples which were subjected to a strain rate of 10 mm min^{-1} using an Instron 3340 Universal Testing Machine (Instron; Massachusetts) for stress-stain and bond strength measurements. Films were bonded together using a Plasma Cleaner PDC-32G (Harrick Plasma; New York) set to 18 W of RF power for 3 min treatment in a vacuum chamber. Oxygen was added using a flow rate of 393.3 $cm^3\ s^{-1}$ and nitrogen was added using a flow rate of 78.7 $cm^3\ s^{-1}$. The surface activated collagen-PDMS films were pressed together and heated for 1 h at 60 °C to strengthen the bond. T-peel testing was conducted using the Instron machine with a strain rate of 6 mm min^{-1}. Peel strength was calculated as twice the average force applied during the peel (F) divided by the width of the sample (w) (Eq. (3)).

$$Peel\ Strength = 2 \times F/w \tag{3}$$

Contact angle measurements were collected using a CAM100 Contact Angle Meter (KSV Instruments; CT).

Disclaimer

The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of Air Force Research Laboratory, the U.S. Government, or SEMI-FlexTech.

Author contributions statement

B.H. Data curation, Investigation, Writing - original draft

M.F. Writing - original draft; Writing - Review and Editing; Data Curation

J-H.Y. Data Curation

A.K. Conceptualization; Formal Analysis; Methodology; Project administration; Funding acquisition

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We thank Ian Foxton, Julia Schalk, and Suk Chul Yoon for their help in the preparation of the samples. This research is supported by the Small-Scale Systems Integration and Packaging (S3IP) Center of Excellence and SUNY Binghamton Start-Up funds. This material is based on research sponsored by Air Force Research Laboratory under agreement number FA8650-18-2-5402. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation thereon.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.colcom.2020.100301.

References

[1] J. Heikenfeld, A. Jajack, J. Rogers, P. Gutruf, L. Tian, T. Pan, R. Li, M. Khine, J. Kim, J. Wang, Wearable sensors: modalities, challenges, and prospects, Lab Chip 18 (2) (2018) 217–248.
[2] J. Kim, I. Jeerapan, J.R. Sempionatto, A. Barfidokht, R.K. Mishra, A.S. Campbell, L.J. Hubble, J. Wang, Wearable bioelectronics: enzyme-based body-worn electronic devices, Acc. Chem. Res. 51 (11) (2018) 2820–2828.
[3] H.R. Lim, H.S. Kim, R. Qazi, Y.T. Kwon, J.W. Jeong, W.H. Yeo, Advanced soft materials, sensor integrations, and applications of wearable flexible hybrid electronics in healthcare, energy, and environment, Adv. Mater. 32 (15) (2020) e1901924.
[4] Y. Liu, M. Pharr, G.A. Salvatore, Lab-on-skin: a review of flexible and stretchable electronics for wearable health monitoring, ACS Nano 11 (10) (2017) 9614–9635.
[5] A. Bandodkar, J. Choi, S. Lee, W. Jeang, P. Agyare, P. Gutruf, S. Wang, R. Sponenburg, J. Reeder, S. Schon, T. Ray, S. Chen, S. Mehta, S. Ruiz, J. Rogers, Soft, skin-interfaced microfluidic systems with passive galvanic stopwatches for precise chronometric sampling of sweat, Adv. Mater. 31 (32) (2019).
[6] W. Gao, S. Emaminejad, H. Nyein, S. Challa, K. Chen, A. Peck, H. Fahad, H. Ota, H. Shiraki, D. Kiriya, D. Lien, G. Brooks, R. Davis, A. Javey, Fully integrated wearable sensor arrays for multiplexed in situ perspiration analysis, Nature 529 (7587) (2016) 509.
[7] J. Kim, J. Sempionatto, S. Imani, M. Hartel, A. Barfidokht, G. Tang, A. Campbell, P. Mercier, J. Wang, Simultaneous monitoring of sweat and interstitial fluid using a single wearable biosensor platform, Adv. Sci. 5 (10) (2018).
[8] A. Koh, D. Kang, Y. Xue, S. Lee, R. Pielak, J. Kim, T. Hwang, S. Min, A. Banks, P. Bastien, M. Manco, L. Wang, K. Ammann, K. Jang, P. Won, S. Han, R. Ghaffari, U. Paik, M. Slepian, G. Balooch, Y. Huang, J. Rogers, A soft, wearable microfluidic device for the capture, storage, and colorimetric sensing of sweat, Sci. Transl. Med. 8 (366) (2016).
[9] J. Reeder, J. Choi, Y. Xue, P. Gutruf, J. Hanson, M. Liu, T. Ray, A. Bandodkar, R. Avila, W. Xia, S. Krishnan, S. Xu, K. Barnes, M. Pahnke, R. Ghaffari, Y. Huang, J. Rogers, Waterproof, electronics-enabled, epidermal microfluidic devices for sweat collection, biomarker analysis, and thermography in aquatic settings, Sci. Adv. 5 (1) (2019).
[10] S. Sia, G. Whitesides, Microfluidic devices fabricated in poly(dimethylsiloxane) for biological studies, Electrophoresis 24 (21) (2003) 3563–3576.
[11] T. Merkel, V. Bondar, K. Nagai, B. Freeman, I. Pinnau, Gas sorption, diffusion, and permeation in poly(dimethylsiloxane), J. Polym. Sci. B: Polym. Phys. 38 (3) (2000) 415–434.
[12] Y. Heo, L. Cabrera, J. Song, N. Futai, Y. Tung, G. Smith, S. Takayama, Characterization and resolution of evaporation-mediated osmolality shifts that constrain microfluidic cell culture in poly(dimethylsiloxane) devices, Anal. Chem. 79 (3) (2007) 1126–1134.
[13] Y. Choi, M. Gwak, D. Lee, Polymeric cantilever integrated with PDMS/graphene composite strain sensor, Rev. Sci. Instrum. 87 (10) (2016).
[14] S. Sun, Z. Pan, F. Yang, Y. Huang, B. Zhao, A transparent silica colloidal crystal/PDMS composite and its application for crack suppression of metallic coatings, J. Colloid Interface Sci. 461 (2016) 136–143.
[15] C. Ciobanu, A. Groza, S. Iconaru, C. Popa, P. Chapon, M. Chifiriuc, R. Hristu, G. Stanciu, C. Negrila, R. Ghita, M. Ganciu, D. Predoi, Antimicrobial activity evaluation on silver doped hydroxyapatite/polydimethylsiloxane composite layer,

Biomed. Res. Int. (2015) 926513, , https://doi.org/10.1155/2015/926513.
[16] Y. Zhang, M. Ishida, Y. Kazoe, Y. Sato, N. Miki, Water-vapor permeability control of PDMS by the dispersion of collagen powder, IEEJ Trans. Electr. Electron. Eng. 4 (3) (2009) 442–449.
[17] R. Parenteau-Bareil, R. Gauvin, F. Berthod, Collagen-based biomaterials for tissue engineering applications, Materials 3 (3) (2010) 1863–1887.
[18] W. Friess, Collagen - biomaterial for drug delivery, Eur. J. Pharm. Biopharm. 45 (2) (1998) 113–136.
[19] K.S. Rho, L. Jeong, G. Lee, B.M. Seo, Y.J. Park, S.D. Hong, S. Roh, J.J. Cho, W.H. Park, B.M. Min, Electrospinning of collagen nanofibers: effects on the behavior of normal human keratinocytes and early-stage wound healing, Biomaterials 27 (8) (2006) 1452–1461.
[20] H. Hou, B. Li, Z. Zhang, C. Xue, G. Yu, J. Wang, Y. Bao, L. Bu, J. Sun, Z. Peng, S. Su, Moisture absorption and retention properties, and activity in alleviating skin photodamage of collagen polypeptide from marine fish skin, Food Chem. 135 (3) (2012) 1432–1439.
[21] B. van Meer, H. de Vries, K. Firth, J. van Weerd, L. Tertoolen, H. Karperien, P. Jonkheijm, C. Denning, A. IJzerman, C. Mummery, Small molecule absorption by PDMS in the context of drug response bioassays, Biochem. Biophys. Res. Commun. 482 (2) (2017) 323–328.
[22] M. Geerligs, L. van Breemen, G. Peters, P. Ackermans, F. Baaijens, C. Oomens, In vitro indentation to determine the mechanical properties of epidermis, J. Biomech. 44 (6) (2011) 1176–1181.
[23] D. Metin, F. Tihminhoglu, D. Balkose, S. Ulku, The effect of interfacial interactions on the mechanical properties of polypropylene/natural zeolite composites, Compos. A: Appl. Sci. Manuf. 35 (1) (2004) 23–32.
[24] J. Yu, J. Yang, B. Liu, X. Ma, Preparation and characterization of glycerol plasticized-pea starch/ZnO-carboxymethylcellulose sodium nanocomposites, Bioresour. Technol. 100 (11) (2009) 2832–2841.
[25] A. Tropmann, L. Tanguy, P. Koltay, R. Zengerle, L. Riegger, Completely superhydrophobic PDMS surfaces for microfluidics, Langmuir 28 (22) (2012) 8292–8295.
[26] B. Ginn, O. Steinbock, Polymer surface modification using microwave-oven-generated plasma, Langmuir 19 (19) (2003) 8117–8118.
[27] V. Graubner, R. Jordan, O. Nuyken, B. Schnyder, T. Lippert, R. Kotz, A. Wokaun, Photochemical modification of cross-linked poly(dimethylsiloxane) by irradiation at 172 nm, Macromolecules 37 (16) (2004) 5936–5943.
[28] H. She, M. Chaudhury, M. Owen, Silicones and Silicone-Modified Materials, (1998), pp. 322–331.
[29] S. Kim, Y. Zhang, S. Won, A. Bandodkar, Y. Sekine, Y. Xue, J. Koo, S. Harshman, J. Martin, J. Park, T. Ray, K. Crawford, K. Lee, J. Choi, R. Pitsch, C. Grigsby, A. Strang, Y. Chen, S. Xu, J. Kim, A. Koh, J. Ha, Y. Huang, S. Kim, J. Rogers, Superabsorbent polymer valves and colorimetric chemistries for time-sequenced discrete sampling and chloride analysis of sweat via skin-mounted soft microfluidics, Small 14 (12) (2018).
[30] ASTM D1653-13, Standard Test Methods for Water Vapor Transmission of Organic Coating Films, ASTM International, West Conshohocken, PA, 2013.