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Soft Intelligence

Liquids Matter in Compliant Microsystems

SEUNG HEE JEONG

ACTA
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UPPSALA
2016

ISSN 1651-6214
ISBN 978-91-554-9521-3
urn:nbn:se:uu:diva-281281

Dissertation presented at Uppsala University to be publicly examined in Polhemsalen, Ångströmlaboratoriet, Lägerhyddsvägen 1, Uppsala, Wednesday, 11 May 2016 at 09:15 for the degree of Doctor of Philosophy. The examination will be conducted in English. Faculty examiner: Professor Michael D. Dickey (North Carolina State University).

Abstract

Jeong, S. H. 2016. Soft Intelligence. *Liquids Matter in Compliant Microsystems*. *Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology* 1357. 93 pp. Uppsala: Acta Universitatis Upsaliensis. ISBN 978-91-554-9521-3.

Soft matter, here, liquids and polymers, have adaptability to a surrounding geometry. They intrinsically have advantageous characteristics from a mechanical perspective, such as flowing and wetting on surrounding surfaces, giving compliant, conformal and deformable behavior. From the behavior of soft matter for heterogeneous surfaces, compliant structures can be engineered as embedded liquid microstructures or patterned liquid microsystems for emerging compliant microsystems.

Recently, skin electronics and soft robotics have been initiated as potential applications that can provide soft interfaces and interactions for a human-machine interface. To meet the design parameters, developing soft material engineering aimed at tuning material properties and smart processing techniques proper to them are to be highly encouraged. As promising candidates, Gabased liquid alloys and silicone-based elastomers have been widely applied to proof-of-concept compliant structures.

In this thesis, the liquid alloy was employed as a soft and stretchable electrical and thermal conductor (resistor), interconnect and filler in an elastomer structure. Printing-based liquid alloy patterning techniques have been developed with a batch-type, parallel processing scheme. As a simple solution, tape transfer masking was combined with a liquid alloy spraying technique, which provides robust processability. Silicone elastomers could be tunable for multifunctional building blocks by liquid or liquid-like soft solid inclusions. The liquid alloy and a polymer additive were introduced to the silicone elastomer by a simple mixing process. Heterogeneous material microstructures in elastomer networks successfully changed mechanical, thermal and surface properties.

To realize a compliant microsystem, these ideas have in practice been useful in designing and fabricating soft and stretchable systems. Many different designs of the microsystems have been fabricated with the developed techniques and materials, and successfully evaluated under dynamic conditions. The compliant microsystems work as basic components to build up a whole system with soft materials and a processing technology for our emerging society.

Keywords: Liquid, Elastomer, Cross-linking, Liquid alloy, PDMS, Adaptability, Compliance, Interface, Patterning, Printing, Surface energy, Wetting, Composite, Modulus, Stretchability, Viscoelasticity, Thermal conductivity, Contact resistance, Adhesion, Packaging, Integration, Microsystems, Microfluidics, Strain sensor, Thermoelectrics, Inductive coupling, Wireless communication, Stretchable electron-ics, Epidermal electronics, Skin electronics, Soft robotics, Wearable electronics

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ISSN 1651-6214
ISBN 978-91-554-9521-3
urn:nbn:se:uu:diva-281281 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-281281)

Soft intelligence means how soft matter affects its surroundings as a subjective player that can be aware of and adaptively interact with its environment. Intelligence refers both to information gathering soft systems and to smart solutions made possible by the liquids or liquid-like matter in a system. Here, liquid denotes the liquid alloy and gel modulus gradients in the elastomer systems of this thesis.

To my lovely family and friends

List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I **Seung Hee Jeong**, Anton Hagman, Klas Hjort, Magnus Jobs, Johan Sundqvist, Zhigang Wu, Liquid Alloy Printing of Microfluidic Stretchable Electronics. *Lab Chip* 12, 4657–4664 (2012).

II **Seung Hee Jeong**, Klas Hjort, Zhigang Wu, Adhesive Transfer Soft Lithography: A Low Cost and Flexible Rapid Prototyping of Microfluidic Devices. *Micro and Nanosystems* 6, 42-49 (2014).

III **Seung Hee Jeong**, Klas Hjort, Zhigang Wu, Tape Transfer Printing of a Liquid Metal Alloy for Stretchable RF Electronics, *MDPI Sensors* 14, 16311-16321 (2014).

IV **Seung Hee Jeong**, Klas Hjort, Zhigang Wu, Tape Transfer Atomization Patterning of Liquid Alloys for Microfluidic Stretchable Wireless Power Transfer. *Sci. Rep.* 5, 8419 (2015).

V **Seung Hee Jeong**, Zhigang Wu, Stretchable Wireless Power Transfer with a Liquid Alloy Coil. *Micro Electro Mechanical Systems (MEMS), 2015 28th IEEE International Conference on* Estoril, 18-22 Jan. 2015, pp. 1137-1140.

VI **Seung Hee Jeong**, Si Chen, Jinxing Huo, Erik Kristofer Gamstedt, Johan Liu, Shi-Li Zhang, Zhi-Bin Zhang, Klas Hjort, Zhigang Wu, Mechanically Stretchable and Electrically Insulating Thermal Elastomer Composite by Liquid Alloy Droplet Embedment. *Sci. Rep.* 5, 18257 (2015).

VII **Seung Hee Jeong**, Shuo Zhang, Klas Hjort, Zhigang Wu, Soft, Stretchable and Sticky PDMS tuned for epidermal electronics. Submitted to *Adv. Mater.*

VIII **Seung Hee Jeong**, Javier Cruz, Si Chen, Laurant Gravier, Johan Liu, Zhigang Wu, Klas Hjort, Shi-Li Zhang, Zhi-Bin Zhang, Stretchable thermoelectric generators metallized with liquid alloy. Submitted to *J. Micromech. Microeng.*

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Author´s Contribution

Paper I Author contributed to a part of planning, design, experiment, and the major part of characterization, analysis, and the major part of discussion and writing.

Paper II Author contributed to most of planning, design, experiment, characterization, analysis and a part of discussion and writing.

Paper III Author contributed to most of planning, design, experiment, characterization, analysis and the major part of discussion and writing.

Paper IV Author contributed to most of planning, design, experiment, characterization, analysis and the major part of discussion and writing.

Paper V Author contributed to most of planning, design, experiment, characterization, analysis and most of discussion and writing.

Paper VI Author contributed to most of planning, design, experiment, characterization, analysis and most of discussion and writing.

Paper VII Author contributed to most of planning, design, experiment, characterization, analysis and the major part of discussion and writing.

Paper VIII Author contributed to most of planning, design, experiment, characterization, analysis and the major part of discussion and writing.

List of Related Contributions

Related papers which are not included in this thesis due to being covered with the appended papers or out of scope of this thesis are listed.

I Byung-Wook Park, Meysam Pazoki, **Seung-hee Jeong**, Erik M. J. Johansson, Anders Hagfeldt, Gerrit Boschloo, Influence of Metalized PEDOT Counter Electrode for Dye Sensitized Solar Cell employed Cobalt (II/III) Complex and I-/I3 Redox Shuttles. *ACS Appl. Mater. Interfaces* 6, 2074–2079 (2014).

II Patrik Ahlberg, **Seung Hee Jeong**, Mingzhi Jiao, Zhigang Wu, Ulf Jansson, Shi-Li Zhang, Zhi-Bin Zhang, Graphene as a Diffusion Barrier in Galinstan-Solid Metal Contacts. *IEEE Trans. Electron Devices* 61, 2996-3000 (2014).

III **Seung Hee Jeong**, Klas Hjort, Zhigang Wu, Batch produced microfluidic stretchable printed circuits for wireless systems. *Micromechanics and Microsystems Europe (MME)*, Istanbul, Turkey, 31 Aug.-3 Sep. 2014 (Poster, Best poster prize).

IV Zhigang Wu, Klas Hjort, **Seung Hee Jeong**, Microfluidic Stretchable Radio Frequency Devices. *Proc. IEEE* 99, 1-15 (2015).

V **Seung Hee Jeong**, Francisco Javier Pérez Cruz, Zhigang Wu, Zhi-Bin Zhang, Shi-Li Zhang, Klas Hjort, Soft bendable thermoelectric generator for uneven surface implementation. *Micromechanics and Microsystems Europe (MME)*, Toredo, Spain, 20-23 Sep. 2015 (Poster).

VI **Seung Hee Jeong**, Si Chen, Jinxing Huo, Zhigang Wu, Zhi-Bin Zhang, Johan Liu, Kristofer Gamstedt, Shi-Li Zhang, Klas Hjort, Thermal elastomer composites for soft transducers. S*olid-State Sensors, Actuators and Microsystems (TRANSDUCERS), 2015 Transducers - 2015 18th International Conference on,* Anchorage, AK, 21-25 Jun. 2015, pp. 1873-1876.

VII **Seung Hee Jeong**, Shou Zhang, Klas Hjort, Zhigang Wu, Sticky elastomer composites for microfluidic stretchable sensor patches. *MRS Fall 2015*, Boston, MA, 29 Nov.-4 Dec. 2015 (Oral).

VIII Zhigang Wu, **Seung Hee Jeong**, Klas Hjort, Stretchable Thermal Conductor embedding Liquid Alloy Fillers for Thermal Applications, *ASME International Mechanical Engineering Congress and Exposition (IMECE)*, Phoenix, AZ, 11-17 Nov. 2016, *accepted.*

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Contents

Soft Technology 21
- Towards a Soft and Dynamic Life 21
- Research Background 23
- Thesis Overview 32

Soft Materials and Characteristics 36
- Soft Materials 36
- Liquid Wetting on a Soft Surface 39
- Liquid-Soft Solid System 41
- Soft Thermal Contact 43
- Stretchable Elastomer Network 45
- Soft Surface Adhesion 48

Soft Material Processing 50
- Liquid Alloy Patterning 50
- Mechanical Property Tuning of PDMS 51

Compliant Microsystems 52
- Stretchable Strain Sensor 52
- Compliant Thermoelectric Generator 54
- Deformable Wireless Systems 55

Characterizations of Soft Materials and Devices 57
- Material and Pattern Characterizations 57
- Device Characterizations 59

Summary of Papers 61
- Liquid Alloy Patterning (Papers I-IV) 61
- Thermal Elastomer Composite (Papers VI, VIII) 62
- Soft, Stretchable and Sticky PDMS (Papers VII) 63
- Liquid Alloy Interface (Papers VI, VIII) 64
- Stretchable Sensors (Papers VI, VII) 65
- Thermoelectric Generator (Papers VI, VIII) 66
- Wireless Communication (Papers I, III-V) 67

Concluding Remarks and Outlook 68

References 71

Svensk Sammanfattning.....87
Self-Reflection.....90
Acknowledgements.....90

Abbreviations

AFM	Atomic Force Microscope
ASTM	American Society for Testing and Materials
BLT	Bond Line Thickness
CNT	Carbon NanoTube
DEAP	Dielectric ElectroActive Polymer
DUT	Device Under Test
GF	Gauge Factor
PDMS	PolyDiMethylSiloxane
PEIE	PolyEthylenImine, Ethoxylated solution
RFID	Radio Frequency IDentification
RTD	Resistance Temperature Detector
SEM	Scanning Electron Microscope
STEG	Stretchable ThermoElectric Generator
S3-PDMS	Soft, Stretchable and Sticky PDMS
TC	ThermoCouples
TE	ThermoElectric
TEG	ThermoElectric Generator
TEC	Thermal Elastomer Composite
TGA	ThermoGravimetric Analysis
TIM	Thermal Interface Material
VACNT	Vertically Aligned Carbon NanoTube
WPT	Wireless Power Transfer

Nomenclature

θ	Contact angle (°)
γ	Surface tension (N/m)
h	Droplet height (m)
g	Gravitational acceleration (m/s^2)
ρ	Density (kg/m^3)
ε	Engineering strain
E	Tensile modulus (Young´s modulus) (Pa)
f	Volume fraction, Force (N), or Frequency (Hz)
ν	Poisson´s ratio, Specific volume (m^3/kg), or volume fraction
G, μ	Shear modulus (Pa)
K	Bulk modulus (Pa)
U	Internal energy (J)
L	Length (m)
V	Volume (m^3 or l)
T	Temperature (°C)
S_r	Swelling ratio
G_f	Gel fraction
n	Number of network chain segment bounded by cross-links
M_c	Chain molecular mass
X	Flory interaction term
R	Gas constant (J/mol·K)
α	Thermal diffusivity (m^2/s)
C_p	Specific heat capacity (J/Kg·K)
κ	Thermal conductivity (W/m·K)
Q	Heat flux (W/m^2)
R_{th}	Thermal resistance (K/W)
$R_{th,c}$	Thermal contact resistance ($K/m^2 \cdot W$)
t	Thickness (m)
φ	Volume fraction
S	Seebeck coefficient (V/K)
σ	Electrical conductivity (S/m)
ZT	Figure of merit
I	Electric current (A)
L	Inductance (H)
ω	Angular frequency (rad/s)

List of Figures and Tables

List of Figures

Figure 1. An inflatable robot consoling a boy with a soft hug.

Figure 2. Soft technology in wearable electronics and soft robotics. (a) A wireless smart sensor patch monitoring a body condition, (b) jumping soft robot powered by combustion and (c) soft gripper controlled by pneumatic actuation. (Figures are adapted with permission from MC10, Inc., Wyss Institute and Softrobotics, Inc., respectively.)

Figure 3. Various types of stretchable conductors made of (a) a wavy shape thin film metal, (b) a serpentine shape thin film metal, (c) a carbon nanotube composite (d) a Ag nanowire composite, (e) a hydrogel and (f) an ionogel.

Figure 4. Liquid alloy patterning methods with different approaches. (a) Liquid alloy injection process, (b) scribing or laminating process on a selective wetting template, (c) imprinting with a structured stamp, (d) direct writing with a dispenser, (e) direct writing with a pressuring ball point pen, and (f) pressurized direct writing on an embedded liquid alloy template.

Figure 5. Schematics of soft-lithography processes. (a) Replica molding (REM), (b) micro transfer molding (μTM), (c) micromolding in capillaries (MIMIC), and (d) solvent assisted micromolding (SAMIM).

Figure 6. Compliant devices and systems for emerging applications. (a) stretchable strain sensors implemented on a suit to monitor human leg movement, (b) pneumatic soft actuators to assist finger force for grabbing, (c) implantable stretchable electrode for stimulating an injured spinal cord and (d) a soft gripper based on dielectric elastomer actuators.

Figure 7. Physical components for compliant microsystems and the research scope of this thesis.

Figure 8. A liquid alloy (Galinstan) puddle spread on the S3-PDMS at room temperature in air.

Figure 9. A PDMS sample stretched by hands.

Figure 10. The chemical structures of the two component, silicones base and cross-linker, of PDMS.

Figure 11. The chemical structure of PEIE.

Figure 12. Schematics of liquid wetting on a solid surface.

Figure 13. Liquid alloy droplets (side view) on (a) PDMS, (b) VACNT surface and (c) liquid alloy line patterns on PDMS, printed by spraying and tape transfer masking.

Figure 14. Thermal elastomer composite (TEC), (a) a schematic drawing of liquid inclusion, (b) micrographs from optical microscope, of embedded liquid alloys in the PDMS (b) with 10 wt% fraction and (c) 75 wt% fraction.

Figure 15. Thermal resistance vs. BLT by the ASTM-D5470 method.

Figure 16. Network structures with cross-links and entanglements. Cross-linked networks of (a) a high density, (b) a low density and (c) a heterogeneous density. The red dots indicate cross-linking. The short arrow marks a typical mesh size, whereas the long arrow indicates the typical length scale of spatial variation of crosslinking density.

Figure 17. A PDMS piece (left) and its swollen state (right).

Figure 18. Schematic drawing of adhesion principles. (a) van der Waals interaction, (b) hydrogen bonding, (c) electrostatic interaction and (d) polymer chain dangling end interlocking.

Figure 19. Schematics of printing processes by (a) rolling and (b) spraying and the patterns from (c, d) the respective technique. (The scale bar indicates 100 μm.)

Figure 20. Material processing for (a) a TEC and (b) an S3-PDMS, (c) the fabricated sample of (c) the TEC and (d) the S3-PDMS.

Figure 21. A stretchable strain sensor adhered on finger skin by the self-adhesive S3-PDMS.

Figure 22. Stretchable thermoelectric generators. (a) The structure of the STEG and (b) the fabricated STEG on a hand and pipe.

Figure 23. A wireless power transfer system. (a) Schematic drawing and (b) the fabricated stretchable WPT system.

Figure 24. The automatic stretching setup for tensile strain and cycling.

Figure 25. The thermoelectric measurement setup. (a) Schematics of the DUT and (b,c) photographs of the thermoelectric measurement setup.

List of Tables

Table 1. Properties of various types of stretchable conductors.

Table 2. Comparison of liquid ally patterning processes.

Table 3. Mechanical properties of several elastomers.

Table 4. Several approaches for mechanical property tuning of PDMS.

Table 5. Adhesion forces of several sticky materials.

Table 6. Thermal properties of several thermal interface materials.

Table 7. Properties of liquid metals and liquid alloys.

Soft Technology

Towards a Soft and Dynamic Life

Human life has been historically governed by in turn nature, philosophy, art and currently, technology. In modern era, “Engineering” with strong supports of “scientific investigations”, has changed our life style and society. In the history, people initiate needs to make inventions or scientific breakthroughs, such as printing techniques for effective distribution of knowledge, power plants and machines for high productivity, vehicles for time-effective delivery, electronic devices for computing and telecommunication, food or medicine for better quality of life, novel materials such as polymers or nanomaterials. Therefore, the direction of new technology development should be considered in society for a human-driven life, which will strongly affect our life style.

As one of the potential direction to go for, our society can proceed towards a “soft technology”-driven life. The advantages and disadvantages of the soft technology need to be discussed in order to have a clear continuation of the approach. Soft technology can pave the way so that people can ergonomically communicate with their environment for better work and play in everyday life. Soft technology has the potential to provide a smart interface for either human-to-human or human-to-machine. For instance, an animation movie, Big Hero 6 (The Walt Disney Company, 2014), Figure 1, is a forecast of the soft technology with soft materials where an inflatable robot can build a warm relationship with a human being.

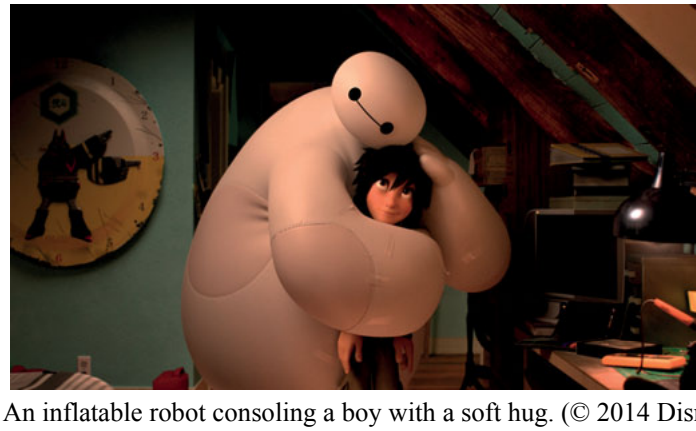

Figure 1. An inflatable robot consoling a boy with a soft hug. (© 2014 Disney)

Biotechnology and robotics for a better human life approach to soft technology based on soft materials because they need to be contacted with soft objects such as living systems, Figure 2. Several examples related to the soft technology have been recently reported, which have attracted engineers´ interests, *e.g.*, artificial skin that can mimic human skin[1-3], artificial muscle that can be robustly controlled with feedback of sensory motor loops[4], organ-on-a-chip that allows in-vitro drug test[5], artificial organs that can make up for malfunctions[6-8], soft robotic gripper that can handle a fragile and soft object without damage[9,10], an exoskeletal glove or suit that can assist a body motion[11], an implantable biomedical electrode that can sense and stimulate a neural system[12], wireless skin sensor that can monitor body conditions[13-16] and a soft robot that can behave like a frog, an octopus or a micromachine[17-20]. In this sense, soft technology will strongly support our coming era by providing remarkable assistance to human life, which has not been shown before in a hard material-based system. Such soft machines consist of soft materials, mainly with liquids and polymers. Soft components give a soft interface to a target object, such as a human, machine or environment. Soft touch or implementation that can provide conformal, compliant, deformable and adaptable interface is beneficial in the case of a human engaged dynamic situation. To realize soft technology[21-24], a software module is definitely required, such as Internet of Things (IoT), artificial intelligence, machine learning and object recognition.

Without doubt, an important part of the soft technology innovations must originate from soft materials and processing technologies. Soft materials including liquids, polymers, and even metals when designed with certain geometry, have a great opportunity to be exploited to realize compliant systems. For the first step, hybridization of soft and hard materials is inevitable. Therefore, the interface between heterogeneous stiffness components plays an important role since we have to employ soft materials together with hard materials in the same system.

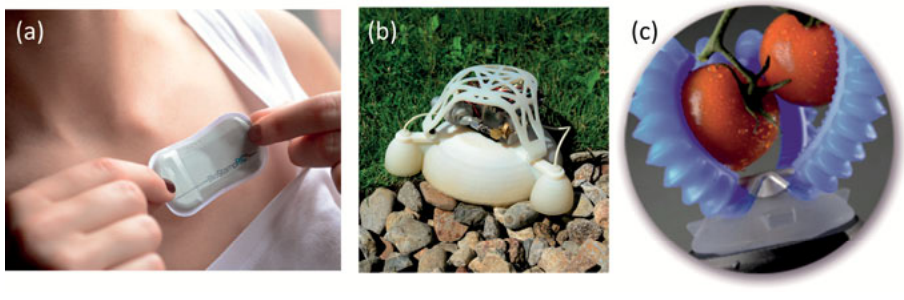

Figure 2. Soft technology in wearable electronics and soft robotics. (a) A wireless smart sensor patch monitoring a body condition, (b) jumping soft robot powered by combustion and (c) soft gripper controlled by pneumatic actuation. (Figures are adapted with permission from MC10, Inc., Wyss Institute and Softrobotics, Inc., respectively.)

Engineering always concerns the smart combination of design, materials and processing to reach target performance of a system. As examples demonstrated by J. A. Rogers´ group in University of Illinois, Urbana-Champaign (USA), stretchable epidermal electronics, which is based on a thin film metal conductor allowing a large strain by designing a wavy or serpentine shape and a stress-free, neutral plane in silicone elastomer packaging, has used hybridization of different stiffness materials in processing as well as in devices.[25] The approach is based on combination of the conventionally well-developed silicon-based technology and soft materials. At the interface of a thin film and a silicone surface, many forces such as van der Waals interaction, hydrogen bonding and electrostatic forces work for the adhesion.

For a millimeter scale system, stiffness gradients are important at the interface from soft (compliant) to hard materials.[17,26] Depending on the structure and performance of a compliant system, reversible adhesion or permanent bonding is necessitated at the interface. Otherwise, the compliant system cannot work properly because of possible delamination, breaking or improper compliance to a target surface at the interface. For further expanding the possibility and potentials of the soft technology, fully soft machines consisting of only soft materials will be the next step.

Research Background

To realize a compliant microsystem beyond a flexible system, soft and stretchable materials and their processing techniques[25,27-29] are necessary to produce the demanding characteristics. The structure consists of a stretchable conductor, interconnect, packaging and functional blocks such as sensors, actuators, power sources and circuitry. Here, the related research on soft materials, processing and devices is introduced to give the research background.

Stretchable conductor. A stretchable conductor can be a metal, conductive composite or liquid that can flow electric current without breaking under high strain and dynamic conditions. Many stretchable conductors, Figure 3, are reported with various compliant proof-of-concept devices, such as strain sensors[30-33], pressure sensors[34,35], a thermal sensor and actuator[36], a mechanical actuator[37], organic transistors[38-40] and antennas[41-44]. A thin film metal can be strained with being conductive by electron tunneling across a nanometer gap when it is stretched even though it becomes cracked. In this case, the strain is limited to less than 0.2.[45,46]

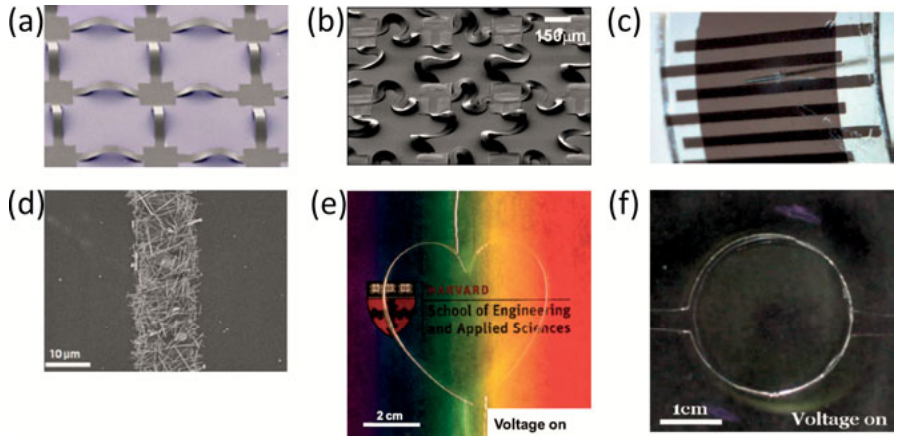

Figure 3. Various types of stretchable conductors made of (a) a wavy shape thin film metal, (b) a serpentine shape thin film metal, (c) a carbon nanotube composite (d) a Ag nanowire composite, (e) a hydrogel and (f) an ionogel. (Figures are adapted with permission from ref. (a) 46. Copyright 2008 Wiley, (b) 47. Copyright 2008 National Academy of Sciences, (c) 48. Copyright 2015 Wiley, (d) 49. Copyright 2015 American Chemical Society (ACS), (e) 50. Copyright 2013 the American Association for the Advancement of Science (AAAS) and (f) 51. Copyright 2014 ACS)

Table 1. Properties of various types of stretchable conductors.

	Thin film metal	**CNT composite**	**AgNW composite**	**Ionogel**	**Liquid alloy**
Material	Au	SWNT+ PDMS[a]	AgNW[b]+ PDMS	AA+PEGDA+ $[C_2mim][EtSO_4]$[c]	eGaIn
Stretchability	20% wavy, 300% serpentine	134%	50%	400%	Unlimited
Electrical conductivity (S/cm)	44.2×10^{6}[d]	58 at 0%, 6 at 134%	8,130 at 0%, 5,285 at 50%	0.22	3.4×10^{4}
Requirement	Thin film Patterning	CNT Dispersion	AgNW Dispersion	UV Exposure	Encapsulation
Reference	46,52	53	54	51	55

a. PDMS (Polydimethylsiloxane); b. NW (nanowire); c. AA (acrylic acid), PEGDA ((ethylene glycol) diacrylate), $[C_2mim][EtSO_4]$ (1-ethyl-3-methylimidazolium ethylsulfate); d. the value is from an element periodic table.

Later, a thin film metal (tens of or hundreds of nanometers) with a wavy shape[46,47,56,57], serpentine shape[52,58,59], Kirigami design[60] or on a prestretched substrate[61] can be reversibly stretched with a large strain in an elastomer packaging. Carbon nanotube (CNT) composites[48,53,62] or metallic nanowire composites[49,54,63-65] work as stretchable conductors. Ionic liquids in a microfluidic channel[50,66] have been demonstrated as a stretchable conductor. Re-

cently, hydrogels[50,67] and an ionogel[51] showed potentials as stretchable conductors with high stretchability.

As one of the stretchable conductors, liquid alloys, such as eGaIn[68,69] or Galinstan®[55,70,71], have a high potential with high electrical conductivity and high stretchability, compared to stretchable thin films or composite conductors. The liquid alloys allow unlimited reversible strain, by following a deformation of a fluidic channel, with negligibly small mechanical stress. Fortunately, the liquid alloys can slide at the interface contacted to heterogeneous surfaces of integrated components, which provides reliable contacts under dynamic conditions. Mechanical properties of several stretchable conductors are compared in, Table 1.

Liquid alloy patterning techniques on silicone elastomer substrates or inside it have been suggested by many groups, Figure 4. Liquid alloy injection into microfluidic channels is widely applied.[30,72] Contact type printing schemes through a hard mask showed high resolution patterning.[73-75] A stamping (imprinting) with a silicone stamp head[76,77], direct writing (dispensing)[78,79], pressurizing on embedded liquid alloy templates[80,81], 3D printing with a syringe pump[82], and non-contact type printing such as spraying through a hard mask[83] have been successfully demonstrated with useful liquid alloy pattern quality. In the processing techniques, resolution, definition, geometry uniformity of a pattern, a process speed and yield are needed to be optimized. For liquid patterning, a microfluidic channel or cavity is necessary for keeping a liquid pattern, as it is patterned, in a soft and stretchable medium. Several processing techniques for liquid alloy patterning are compared in Table 2.

Table 2. Comparison of liquid ally patterning processes.

	Injection	**Scribing (Laminating)**	**Imprinting (Stamping)**	**Direct Writing**	**Pressurized writing**
Requirement	Microfludic channel	Template, Hard mask	Soft stamp	Syringe, Pump, Auto-stage	Liquid alloy template
Resolution	10 μm	200 μm	2 μm	100 μm	20 μm
Pros	Clear pattern shape	Selectivity	Resolution	Design change adaptability	Application adaptance, high resolution
Cons	Leakage	Lithography	High resistance	Equipment	Stretchability, Leakage
Reference	30,66	73,75	76,77	78,79	80,81

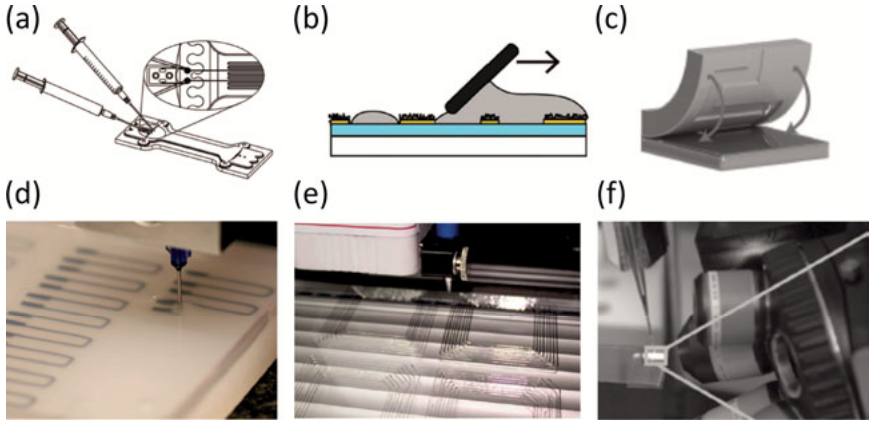

Figure 4. Liquid alloy patterning methods with different approaches. (a) A liquid alloy injection process, (b) a scribing or laminating process on a selective wetting template, (c) an imprinting with a structured stamp, (d) a direct writing with a dispenser, (e) a direct writing with a ball point pen, and (f) a pressurized direct writing on an embedded liquid alloy template. (Figures are adapted with permission from ref. (a) 30. Copyright 2008 Wiley, (b) 75. Copyright 2008 National Academy of Sciences, (c) 76. Copyright 2015 Wiley, (d) 78. Copyright 2015 ACS, (e) 84. Copyright 2013 AAAS and (f) 81. Copyright 2014 ACS)

Soft-lithography. Soft material (polymer, especially silicone) processing needs to be different from hard material processing because soft material properties are quite different, such as being soft, viscous, sticky and melting at a low temperature. Even for a conventional rubber processing method such an extrusion process may not be appropriate for soft material processing for compliant microsystem fabrication because the systems have to include heterogeneous materials. From the concept of the lithography techniques, which have been well developed for silicon microelectronics, soft-lithography schemes for soft material patterning or structuring with a few kinds of silicones[28,85-87] were initiated from G. M. Whitesides´ group at Harvard University (USA). Soft-lithography includes molding, transferring, capillary flowing, self-assembly, layer-by-layer structuring, curing and bonding. Liquid-like behavior of a silicone prepolymer, such as wetting and flowing, play an important role in the process, with surface affinity of heterogeneous materials. In addition, soft-lithography is fairly compatible with the conventional silicon processes. Soft-lithography techniques that are frequently used are summarized in Figure 5.

Elastomers. An elastomer, most often a rubber, is a unique material that can be stretched and turned back to its original shape when an external force is removed. As a compliant packaging material, an elastomer is a promising material to fabricate compliant microsystems. A soft and stretchable material and structure is faced to dynamics in operating conditions, such as bending, pressing, stretching and twisting at different frequencies. To design a com-

pliant microsystem with an elastomer, the mechanical characteristics of elastomers should be understood. Elastomers have, for instance, a non-linear stress-strain relationship, a Poisson´s ratio close to 0.5 and a first large hysteresis in the stress-strain curve. A long-time maintained strain causes a creep that leads to a permanent deformation even in an elastomer. For the soft technology, mechanical property tuning of elastomers proper to applications is vital because "soft" refers to its mechanics.

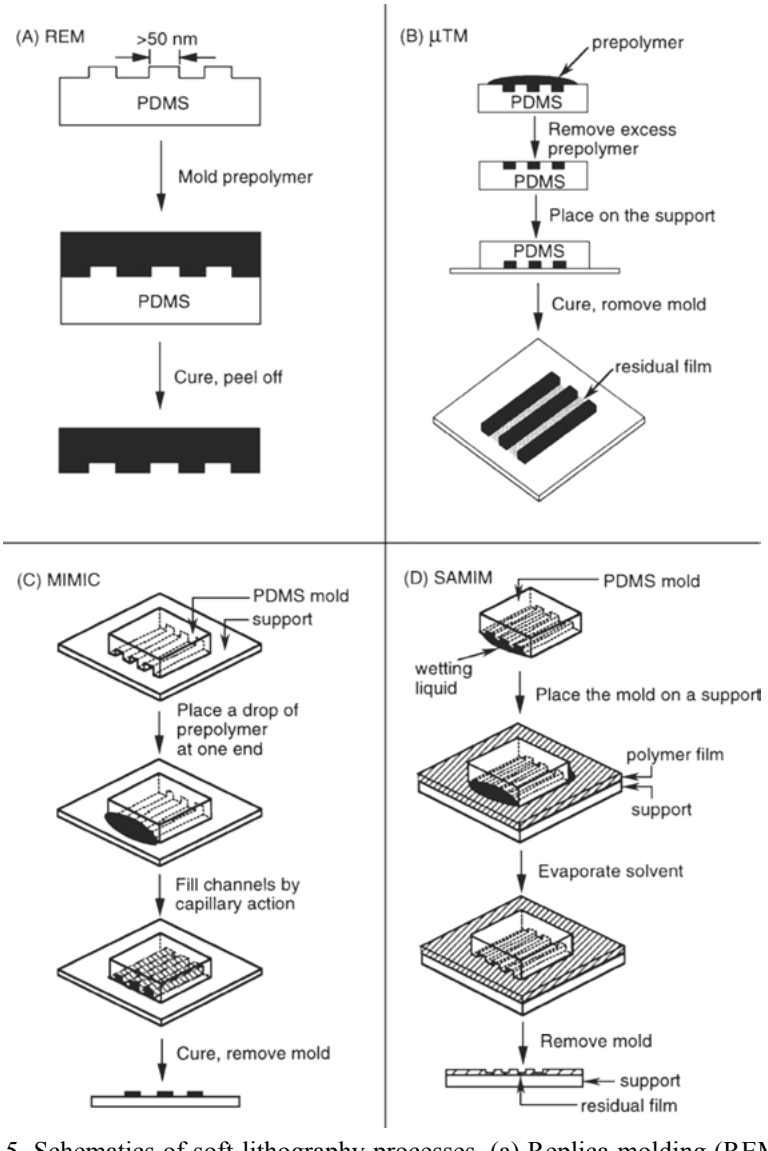

Figure 5. Schematics of soft-lithography processes. (a) Replica molding (REM), (b) micro transfer molding (μTM), (c) micromolding in capillaries (MIMIC), and (d) solvent assisted micromolding (SAMIM). (Figure is adapted with permission from ref.[28]. Copyright 1998 Annual Review of Materials Science)

Table 3. Mechanical properties of several elastomers.

	PDMS (Elastosil RT601)	Hydrogel (alginate+polyacrylamide)	SEBS (Duftec H1221)	Silicone (EcoFlex 00-30[a])	Acryl (VHB 4920[b])
Stretchability	>100%	1,100%	>900%	900%	-
Elastic modulus (MPa)	6	0.029~0.156	1~9.5	1.4	1.1
Density (g/cm^3)	1.02	-	0.89	-	0.8
Reference	88	67	89	90	91

a. EcoFlex 00-30 is a silicone elastomer, supplied from Smooth-On, Inc.; b. VHB 4920 is an acrylic foam tape, supplied from 3M.

In table 3, several elastomeric materials are compared in mechanical aspects. Polydimethylsiloxane (PDMS)[88,92] has been widely used for microfluidics, stretchable electronics and soft robotics. Poly[styrene-b-(ethyleneco-butylene)-b-styrene] triblock copolymer (SEBS)[89,93-95] is highly stretchable up to 10 times the original length, reversibly. Hydrogels can be a good solution in an aquatic environment such as human body or oceans.

Elastomer composite. Composite materials can have multi-functions from a matrix and embedded fillers. Fillers are chemically different components for the matrix. If an elastomer is used as a matrix, the composite system can be elastic. Simultaneously, the fillers, which can be solid particles or liquids, can provide additional properties to the elastomer composite. Mechanical stiffness, electrical conductivity, magnetic properties, thermal properties and dielectric properties of fillers can be granted to the elastomer. The mixing ratio and processing conditions are critical to control the composite properties. For example, an elastomer can be electrically conductive with carbon nanotubes[96] or metallic nanowires, when the filler concentration is above a percolation threshold, where the conductivity is considerably increased. The composite becomes thermally conductive as well as mechanically stiffer.[97] Many trials to make stretchable, electrical conductors or high dielectric insulators have been done for stretchable sensors and soft actuators, respectively. Chemically functionalized fillers to control surface energy can be potential candidates to improve the interface between fillers and a matrix. Understanding the interface of different materials is necessary to estimate the behavior of the composite.[98]

Elastomer tuning. Many elastomers are studied for tuning mechanical properties such as elastic modulus, toughness, stretchability, hysteresis, Poisson´s

Table 4. Several approaches for mechanical property tuning of PDMS.

Tuning Methods	Curing temperature	Thinner	Photo-inhibitor	Heterogeneous polymer	Bottle brush
Stretchability	93~50%	180%	140%	42~189%	-
Tensile modulus (MPa)	1.32~2.97	1.4~1.8	0.65~2.9	0.05~1.38	0.022
Reference	99	100	101	102	103

ratio, porosity, reversibility and surface adhesion. Several approaches to tune silicone elastomers for mechanical properties have been revealed with methods of; 1) varying a curing process condition such as temperature[99,104], curing time and cross-linker fraction[105]; 2) adding an additive such as thinner[100], moderator[101], inorganic particles[96] or heterogeneous polymers[106-111]; 3) making a porous structure[112,113], and 4) including liquids[114]. All of these ideas are related to a change of the network structure in a micro- and macroscale. In the microscale, polymer chains and their networks can be physically and chemically engineered. The geometrical change of elastomer networks is associated with cross-linking and entanglement. For example, an interpenetrating network[115,116] or a functionally terminated polymer chain[103] tunes an original polymer network structure. An electric field applied curing process or a strain induced drawing process changes the elastomer properties by aligning elastomer chains in the network.[117,118] Liquid or liquid-like soft solid inclusion effectively alters mechanical properties of an elastomer. It becomes softer and more stretchable due to softness of liquid and heterogeneity of the microstructure.[108,110] In the macroscale, geometrical designs of an elastomer structure can tune mechanical properties, such as porous structure or lattice-like structure.

Sticky surface. The adhesion mechanism is complex, usually combined with several kinds of adhesion force together. Polymeric materials have the advantage of having a high adhesion force due to its conformality and chemical effectors. A compliant surface can have a larger effective contact area to a soft or hard surface compared to a hard-to-hard contact. The reversible adhesion force should be considered for designing a compliant system as well as for manufacturing the system. Biomedical adhesives are potential candidates for use as sticky matter, *e.g.*, adhesives for wound healing and for a biomedical sensor patch implementation on the human body.[119,120] The StickyBot[121,122] inspired by Gecko toe adhesion with a hierarchical structure of nanometer scale fibers[123-125] is an interesting application to be developed for soft robotics. Sticky materials are listed in Table 5.

Table 5. Adhesion forces of several sticky materials.

	Bioadhesive	Gecko seta	Mussel
Adhesion force	5 N	0.4 μN	800 pN
Adhesion line or area	25 mm	2 μm diameter	25 nm diameter
Test surface	Forearm skin	Al	Ti
Measurement	Load cell	MEMS[a] sensor	AFM[b]
Reference	119	123	126

a. MEMS (MicroElectroMechanical Systems); b. AFM (Atomic Force Microscope).

Thermal interface. Thermal contacts, both inside a device structure between heterogeneous materials and outside a device between the device and an implemented surface, are crucial parameters for high heat flux. The interface should have a physical contact area as large as possible as well as high thermal conductivity of materials in thermal device applications, such as thermoelectric (TE) devices, cooling units, light emitting diodes (LED), central processing units (CPU) or power electronics.[127,128] Thermal management is directly connected both to efficiency and to an operation temperature range. In electronic devices, hot spots and uneven temperature distributions deteriorate or destroy device performance. As a solution, a thermal interface material (TIM), such as a thermal grease or pad, has been developed in many different combinations of fillers and soft polymers as composite structures[129]. Recently, vertically aligned CNT (VACNT) arrays[130-133] and graphene sheets[134,135] have been suggested as potential candidates for TIMs. Most of TIMs are soft but a stretchable TIM is unusual except elastomeric connectors (ZEBRA®Fujipoly). TIMs are compared in Table 6.

Table 6. Thermal properties of several thermal interface materials.

	Metallic solder (Al-Zn)	Silicone composite (TC5022[a])	Carbon composite	VACNT (MWNT)	Graphene composite
Thermal resistance ($K \cdot mm^2/W$)	6.3	4	< 1	500	-
Thermal conductivity (W/m·K)	3.7	4	20~40	1.2	5.1
Measurement	ASTM[b] D5470	ASTM D5470	Xenon flash	ASTM D5470	Laser flash
Reference	136	136	137	133	134

a. TC 5022 is a thermal conductive compound, provided by Dow Corning; b. ASTM (American Society for Testing and Materials).

Compliant microsystems. Compliant microsystems have been recently progressed in points of not only the materials and processing technologies, but also device designs. Many kinds of devices are demonstrated in soft and stretchable forms, such as sensors, actuators, wireless components, lighting sources, power sources, biomedical instruments, soft robotic components or soft robots. Soft robotics recently attracts the research society by triggering new ideas for soft materials to be engineered and assembled as soft robotic components, and processing technologies for the soft materials.

One of the niche applications of compliant components is a large stroke measurable strain sensor for human body dynamics to help the design of rehabilitation systems, wearable systems, and soft robots. A liquid alloy-based strain sensor has been tested in a space suit design project of the National Aeronautics and Space Administration (NASA, USA)[138,139] and in an exoskeletal suit design and control for the Defense Advanced Research Projects Agency (DARPA, USA)[140,141].

Soft actuators operated by thermal stimulation with shape memory polymers (SMPs)[142-144] or liquid crystal elastomers/polymers[145,146] showed potentials to soft actuation, *e.g.*, for an origami robot application[147,148]. For actuation in liquid environment, polymers can be employed such as a conjugated polymer stimulated by electrochemical potential[149,150] and a hydrogel swollen by capillary force and thermal energy[151]. A dielectric electroactive polymer (DEAP) actuator[152-154] is widely studied for high speed and electrically controllable soft actuators but it needs a high electric field and it only works for a small displacement. Ionic polymer metal composite (IPMC) actuators[155] can work at a lower energy compared to a DEAP actuator, but it react slowly.[156,157] Carbon based materials have potential to be applied to actuating systems, such as carbon nanotube yarn stimulated by multiple excitation methods[158], carbon nanotube sheets actuated by electrochemical potential[159] and a graphene composite stimulated by optical exitatoin[160] as additional solutions. An inflatable actuator operated by pneumatic pressure and a soft actuating structure with tendon wires and motors still have a strong position due to its efficiency and controllability, although there is the limitation of carrying a heavy pump or a bulky motor box.[161] A piezoelectric actuator can only work in a small scale and it needs to be integrated in a compliant medium to be soft and stretchable. Therefore, soft technology demands a smart candidate for actuation, which can perform with being high speed, low power consumption, large deformation, lightweight, wireless triggering, soft but stiff enough and reversible. On the other hand, soft actuators basically need geometrical designs that guide motions with a programmed purpose. Hence, the soft actuating material processing ability to fabricate a demanding structure should be developed in parallel with material development. Compliant sensor and actuators for potential applications are shown in Figure 6.

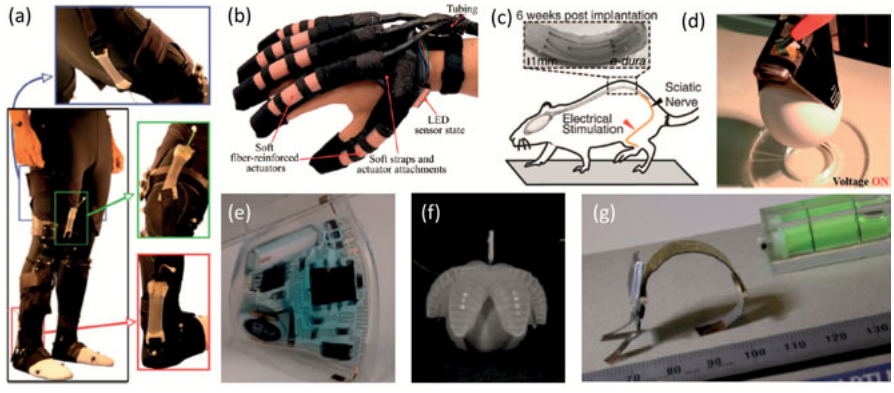

Figure 6. Compliant systems for emerging applications. (a) Stretchable strain sensors implemented on a suit to monitor human leg movement, (b) pneumatic soft actuators to assist finger force for grabbing, (c) an implantable stretchable electrode for stimulating an injured spinal cord, (d) a soft gripper based on dielectric elastomer actuators, (e) a soft microfluidic assembly of sensor, circuit and radio, (f) a soft gripper actuated pneumatic pressure and (g) IPMC actuators working with electrochemical potential. (Figures are adapted with permission from (a) 30. Copyright 2014 IEEE, (b) 141. Copyright 2015 Elsevier, (c) 12. Copyright 2015 AAAS, (d) 152. Copyright 2016 Wiley, (e) 162. Copyright 2014 AAAS, (f) 9. Copyright 2011 Wiley and (g) 163. Copyright 2014 Wiley)

Stretchable power sources, such as capacitors[164], batteries[52], energy harvesters[165] and wireless power transfer (WPT) units[83] have shown promising performance in deformable and stretchy formats, even though the efficiency is reduced compared to a rigid, solid state device. Wireless communication devices, such as an antenna and a radio frequency identification (RFID) tag, have been shown to work under deformable conditions.[41,162] Several examples are listed in Figure 6.

Thesis Overview

A compliant microsystem must be integrated with a soft and stretchable conductor, a functional active component (sensor, actuator, display, energy source, communication unit and circuitry), interconnects and packaging, Figure 7. Sometimes one part can take over another function. Stretchable conductors have been developed with many different materials until now. As a soft and stretchable packaging material, several approaches for tuning silicone-based materials and their tuned variations have been tested for their mechanical properties (modulus, stretchability, hysteresis, adhesion) together with their thermal properties. (Here, we define stretchability with a maximum elongation that can be recovered to the original dimension when the extension force is removed.)

A soft and stretchable conductor and a packaging material are two main players to envisage compliant microsystem applications. For fully soft and highly stretchable devices, a liquid conductor with a multi-functional silicone elastomer is the most promising approach for millimeter scale compliant systems with large deformations due to their high stretchability and deformability. Liquid alloys are conductive enough in high frequency applications and freely deformable without any mechanical damage, such as delamination or cracking. Silicones are totally reversible in stretching and highly stretchable over 100%. In addition, silicone elastomers have processability for microsystems, which can change the phase from liquid to solid before and after curing. To make use of these properties of the soft materials, a liquid hybridization approach combined with a silicone elastomer is adopted to make monolithic, compliant microsystems. Combinations of liquids and elastomers can initiate more functions for emerging systems by engineering them in the material structure and in the processing techniques. In the sense, liquid patterning and silicone property tuning can be the first step.

Liquids are promising candidates for "soft technology". Liquids have amorphous (disordered) atomic and molecular structures in a microscopic scale, which hinder electron and phonon, and thus, have low electrical and thermal conductivity. However, for the same reason, they are freely deformable and adaptable to a surrounding geometry. They can be conformally wet, viscously flowing and mechanically damping. They are somehow hard to handle but there are proper processing methods for them. Therefore, liquids can form compliant systems due to their adaptable and viscous nature. From material properties to system performance, liquids can contribute mainly to the mechanical properties of the systems in the interests of this thesis.

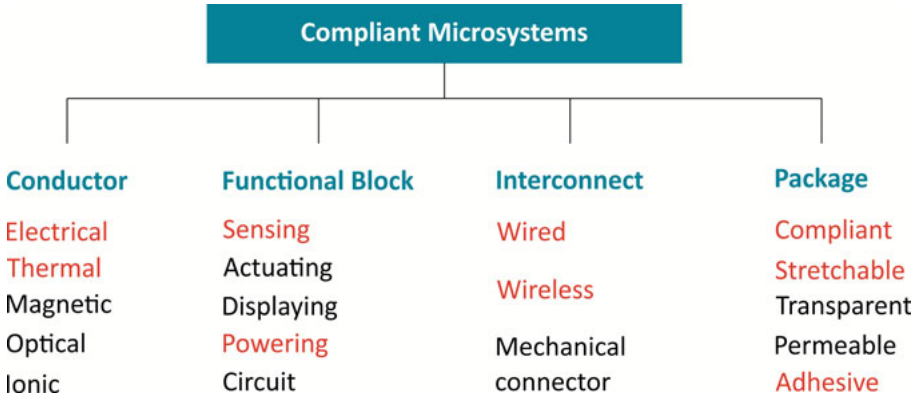

Figure 7. Physical components for compliant microsystems and the research scope of this thesis. (This thesis covers components that are marked in red.)

Two approaches are employed in this thesis. One approach is about *liquid patterning* for a deformable and stretchable liquid conductor and the other is about *multi-functional elastomers* for compliant and stretchable silicone packaging, which have designed functionality. The *soft interface* between soft materials and relatively hard materials are the most challenging points that should be investigated and engineered related to those two categories.

Liquid patterning is challenging due to low viscosity and surface tension of liquid matter. Without needs of any container or template for liquid patterning, a direct patterning can allow more possibilities to make compliant systems for many applications. Usually, liquid patterns should be confined in channels or cavities to form and to maintain shapes, for example, injecting liquids in microfluidic channels. Otherwise, liquid droplets can be localized and immobilized on patterned templates, which has wetting contrasts on the physical and chemical surface structure. Lastly, liquids can be separated by density difference in contact with immiscible liquids. Here, we focus on liquid alloy patterning for compliant microsystem fabrication, which is based on a contact or non-contact printing technique for batch type, large area fabrication.

Multi-functional elastomer composites and blends can be a smart way to possess heterogeneous properties simultaneously in one system. Avoiding complex chemical processing steps, silicone base and cross-linker are mechanically mixed with additive components to have special functions, such as high thermal conductivity or low elastic modulus with keeping the stretchability of elastomers. In this thesis, liquid inclusions or similar effects have been applied for changing elastomer structure. Elastomer networks can support a composite or blend matrix for liquid inclusion in the structure. By selecting the combination of soft materials and processing conditions, the concentration, alignment, gradient and homogeneity of fillers can be controlled for tuning the properties of the composite or the blend. This thesis focuses on a thermal elastomer composite (TEC) including liquid alloy fillers for a stretchable thermal conductor and an elastomer blend tuned in the cross-linking structure for a soft, stretchable and sticky silicone elastomer (S3-PDMS).

Wetting and adhesion of heterogeneous materials are critical points, which engage two surfaces. In a compliant microsystem, the interface becomes more important due to dynamic conditions. Interfaces should be controlled during processing and in a final material or device structure. A soft and stretchable surface can undergo dynamic strains and it needs to be slippery or sticky depending on preferences. Intimate contact helps adhesion, carrier transport or energy transfer. Therefore, a liquid or a highly soft surface is valuable. This thesis focuses on; 1) the liquid alloy wetting, 2) the thermal contact resistance of the liquid alloy and the TEC, and 3) the compliance and the adhesion force of the S3-PDMS.

In summary, the objective of the research in this thesis is to design compliant microsystems with liquids and elastomers, and to understand how they behave. Soft material processing and structuring are done with various approaches for making multi-functional materials and compliant microsystems. Advantages of liquid or liquid-like materials in soft elastomer structures are evaluated with many aspects. The liquid hybridized compliant microsystems based on the liquid alloy and silicone based elastomer are presented.

Soft Materials and Characteristics

Soft Materials

Liquid Alloy. A liquid metal and a liquid alloy, which are in the liquid state around room temperature, have an amorphous structure, *e.g.*, gallium (Ga), mercury (Hg), Cs (Cesium), Field metal (Bi-In-Sn eutectic), Wood metal, (Bi-Pb-Sn-Cd eutectic), Rose metal (Bi-Pb-Sn), Ga-based liquid alloy including eGaIn (Ga-In eutectic) and Galinstan® (Ga-In-Sn eutectic), and FerroFluid (iron nanoparticles in a carrier fluid). Liquidmetal® which was invented by California Institute of Technology (USA) is a solid state metal around room temperature.

Liquid alloys (*e.g.* eGaIn and Galinstan) are known as being non-toxic[166] and Galinstan is used in a commercialized thermometer for human body temperature measurement. The Galinstan, gallium (Ga)-indium (In)-tin (Sn) eutectic alloy including additives (Bi, Sb) which can decrease the melting temperature to -19 °C, is used in this thesis. Reaction, such as amalgamation, corrosion or diffusion of liquid alloys, is possible with metals, such as Al or Au, [167,168] but not with W and Ta because Ga is stable with them.

Metallic liquids around room temperature have a unique property that combines both liquid and metallic nature. Properties from a liquid state and from a metallic state exist in one material. Liquid alloys have a low viscosity, high thermal and high electrical conductivity. The liquid alloys have likely stress-free deformability and fluidity. An oxide skin layer forms on the surface in contact with air. The bilayer system, which is a liquid alloy inside solid gallium oxide (Ga_2O_3) on the surface, behaves in an unusual way as a liquid. The surface can be rounded because of its high surface tension and kept without spreading on a surface when a droplet is less than centimeter in diameter. The surface is semi-plastically deformed due to the oxide skin. The tunneling current density through the oxide skin with silver electrodes has been studied[169-172], which reveals the possibility of electrical applications. The surface reaction with chemical solutions can be worthwhile for liquid alloy droplet actuation.[173-176] The high surface tension of the oxide skin covering the liquid alloy is beneficial for certain situations but not for all the cases. The properties of several liquid metals and liquid alloys are compared in Table 7 and Galinstan on the S3-PDMS is shown in Figure 8.

Table 7. Properties of liquid metals and liquid alloys.

	Unit	Galinstan	eGaIn	Ga	Hg	Cs
Surface tension	m·N/m	670[a]	624	708	480	-
Meltingpoint	°C	-19.0	15.5	29.7	-38.8	28.5
Boiling point	°C	1,300	-	2,400	357	671
Thermal conductivity	W/m·K	16.5	39	40.6	8.5	35.9
Electrical conductivity	S/m	3.46×10^{6}	3.3×10^{6}	3.7×10^{6}	1.04×10^{6}	5×10^{6}
Density	kg/m^3	6,440	6,363	6,095	13,534	1,843
Viscosity	Pa·s	2.4×10^{-3}	1.99×10^{-3}	-	1.53×10^{-3}	-
Reference	-	55	68,177,178	b	b	b

a. A measured value; b. data from the element periodic table.

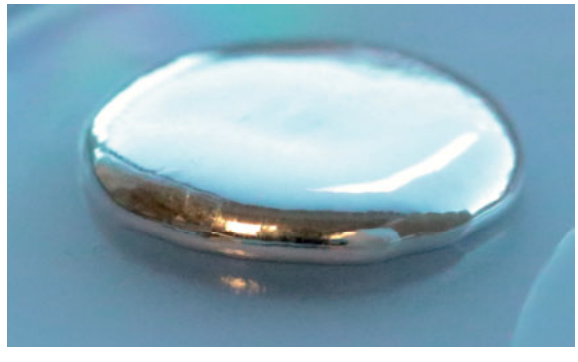

Figure 8. A liquid alloy (Galinstan) puddle spread on an S3-PDMS at room temperature in air. (The diameter is 50 mm.)

Polydimethylsiloxane (PDMS). Silicones are inorganic elastomers that consist of silicon, hydrogen, carbon and oxygen. Silicones are rubber-like materials that are compliant and reversibly stretchable with a large strain.

PDMS is one of the silicone elastomers, which is widely used in many different applications including microfluidic chips, biomedical patches and stretchable electronics because it has a good processability of flowing, coating, casting and curing. It is chemically and thermally stable (T_m -130 °C), electrically and thermally insulating, dielectric and optically transparent. PDMS is gas (N_2, O_2) and water permeable. A 100% stretched PDMS strip is shown in Figure 9.

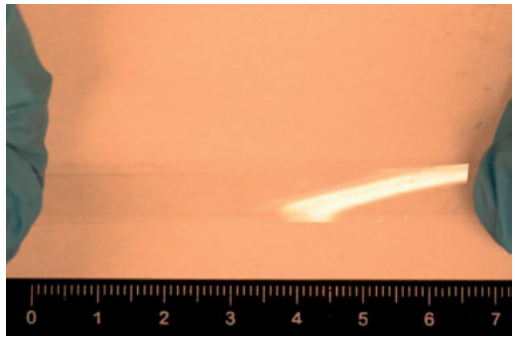

Figure 9. A PDMS sample stretched by hands. (The original length 30 mm.)

PDMS can be cured with two part components, a silicone oligomer (base) and cross-linker, Figure 10, which gives a good processability in many cases. A vinyl functional group in the silicone oligomer is hydrosilylated with a silicon hydride (Si-H) bond in the cross-linker by a Pt- based catalyst, which helps the organometallic reaction between the vinyl group and the hydride bond.[179] The PDMS base (siloxane oligomer) of Sylgard®184 (Dow Corning) consists of dimethyl siloxane, dimethylvinyl-terminated (60 wt%), dimethylvinylated and trimethylated silica (30-60 wt%), occasionally with tetra(trimethylsiloxy) silane (1-5 wt%). The curing agent includes dimethyl, methylhydrogen siloxane (40-70 wt%), dimethyl siloxane, dimethylvinyl-terminated (15-40 wt%) and dimethylvinylated and trimethylated silica (1-5 wt%), occasionally with tetramethyl tetravinyl cyclotetrasiloxane (1-5 wt%).

The curing process can be controlled to tune the mechanical properties of PDMS, such as the elastic modulus and maximum elongation. The PDMS can be more stretchable when cured at low temperatures but the curing time needs to be prolonged. To vary the mechanical stiffness, the density of cross-linking and entanglement can be controlled during the process, for example, by varying the mixing ratio of the two parts. Chemical functionalization (branching, brushing, terminating), additive blending (thinner, silicone oil or photo-initiator) or liquid-like inclusions can work for changing the cross-linking and entanglement network structure.

Surface modification of PDMS for bonding, wetting, functional gradient and adhesion has been studied in real applications for microfluidics, cell culturing and biomedical applications. Plasma treatment is a technique to activate the PDMS surface with a hydroxyl group, which can help surface wetting and bonding of PDMS.

In this thesis, a few PDMS (Elastosil RT601, Sylgard 184 and EcoFle 00-30) are used, developed and tested for making compliant microsystems and for making tuned properties such as elastic modulus, elongation, adhesion as well as thermal properties.

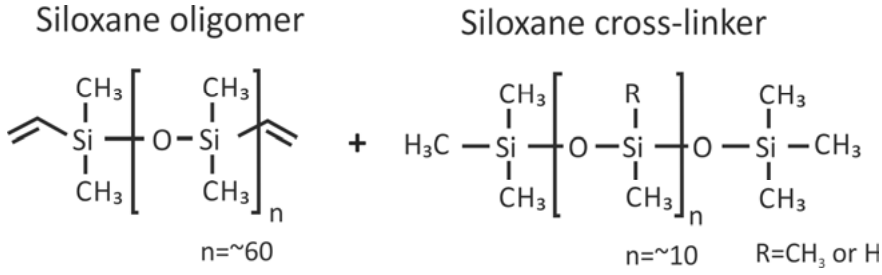

Figure 10. The chemical structures of the two component, silicones base and cross-linker, of PDMS.

Polyethylenimine, ethoxylated (PEIE) solution. PEIE (or EPEI) is an amine-based polymer (C=N units in a backbone) which is terminated with hydroxyl (-OH) groups instead of amino (N-H) groups in polyethylenimine (PEI), Figure 11. Ethoxylated PEI is used as the semi-conducting layer in a photo-voltaic device[180] and for switching the wettability of PDMS[181].

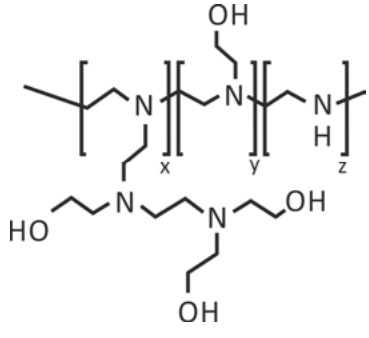

Figure 11. The chemical structure of PEIE.

Liquid Wetting on a Soft Surface

In the small scale regime, from micrometer to nanometer, a material´s behavior and interaction with heterogeneous materials become much more governed by surface related properties, which is dominated compared to the macroscale regime. One of them, wetting has strong influence in small scale systems.[182] Surface energy originated from molecular motions and interactions works at the interface. Liquids can be manipulated with a physically or chemically designed surface.[183-187] For example, self-alignment or self-assembly is used for liquid immobilization and small object positioning.[188] For active manipulation of liquids, electrowetting[189,190] or switchable wetting[181,191] is useful for changing the interface interaction.

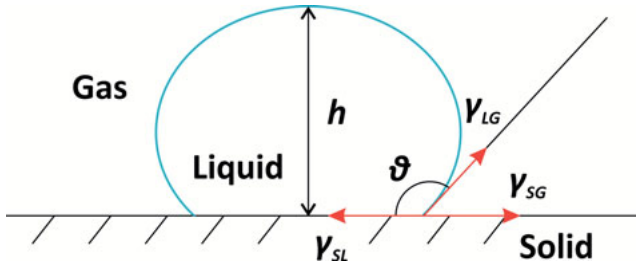

Figure 12. Schematics of liquid wetting on a solid surface.

Dust or water repulsive (antifouling) surface coatings or structuring[192], and selective filtration with differentiated wetting[193] are useful in our real life. Durotaxis is an interesting mechanism on how a surface stiffness gradient can affect local dynamics of a small structure on a soft surface.[194]

Liquid wetting on a solid or soft solid surface[195] is adjusted by a balance of surface tension and the surface energy of interfaced materials (together with gravitational or inertial force under dynamic conditions). A liquid droplet flowing on a solid surface is governed by wetting depending on the volume of liquid.[196] Many different models describe wetting phenomena for various combinations of materials, associated with material properties and micro- or nano-scale geometries of the contact surface.

Young´s equation represents the balance of the surface energy between gas, liquid and solid surfaces.

$$\gamma_{SG} - \gamma_{SL} = \gamma_{LG} \cos\theta \ ,$$

where γ (N/m) is the surface tension, *S*, *L* and *G* denotes solid, liquid and gas, respectively, and θ (°) is the contact angle of the liquid on the solid surface.

The height of a droplet on a solid surface can be derived as

$$h = \sqrt{\frac{2\gamma\ (1-cos\theta)}{g\rho}} \ ,$$

where γ (N/m) is the surface tension of the liquid, g (m/s^2) is the gravitational acceleration and ρ (kg/m^3) is the density of the liquid, Figure 12.

Liquid alloy wetting on a soft elastomer surface is most important for printing-based patterning techniques with a hard mask. The high surface tension of the oxide skin interacts with a silicone surface. It helps the liquid not to spread out on the surface. On the other hand, high surface tension of the liquid alloy does not allow easy handling on the surface. Therefore, a semi-cured PDMS surface and impinged liquid alloy droplets robustly and effectively work for patterning with robust wetting of the liquid alloy on a PDMS surface.

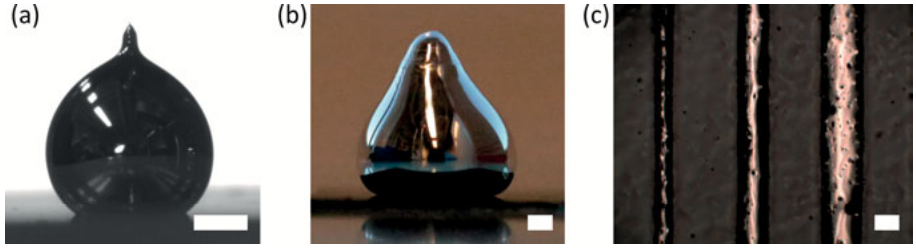

Figure 13. Liquid alloy droplets (side view) on (a) PDMS, (b) VACNT surface and (c) liquid alloy line patterns on PDMS, printed by spraying and tape transfer masking. (The scale bars indicate (a), (b) 1 mm and (c) 100 µm.)

The oxide skin make the liquid alloy behave like a plastic on the surface. The surface can be deformed by mechanical force and the deformed surface maintains the surface topography, such as a cone shape, Figure 13. The wetting is strongly pinned on most of the surfaces and remains the oxide skin residue. The VACNT surface is highly liquid alloy phobic, which can give some unique applications to this combination.

Liquid-Soft Solid System

Polymer composites have been widely developed for many applications in our life. Mechanical and thermal properties have been mainly engineered for everyday use as well as for processing and products. W. Voigt (1889) and A. Reuss (1929) developed the rule of mixtures for a two phase composite system; solid filler inclusion composites. Depending on the directionality of elongated fillers, axial loading parallel to the filler direction gives an upper bound of a property (Voigt model). Material properties, such as elastic modulus, ultimate strength, density, thermal conductivity and electrical conductivity, can be determined by the Voigt model;

$$E_c = fE_f + (1-f)E_m \ ,$$

where E_c is the property (tensile modulus) of the composite system, E_f is the property of fillers, E_m is the property of the matrix and f is the volume fraction of fillers. The Reuss model estimates a lower bound of a material property when transversal loading perpendicular to a filler direction is applied;

$$E_c = \left(\frac{f}{E_f} + \frac{1-f}{E_m}\right)^{-1} \ .$$

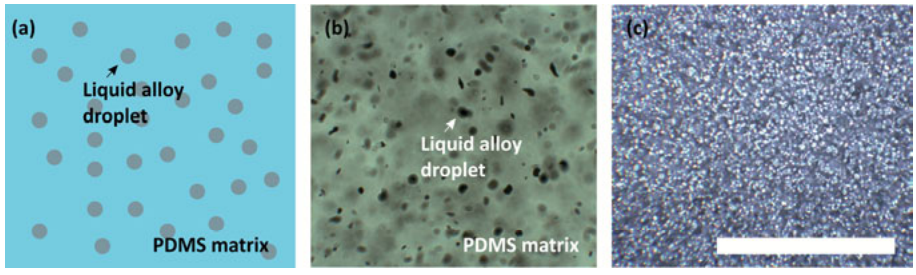

Figure 14. Thermal elastomer composite (TEC), (a) a schematic drawing of liquid inclusion, (b) micrographs from optical microscope, of embedded liquid alloys in the PDMS (b) with 10 wt% fraction and (c) 75 wt% fraction. (The scale bar indicates 100 μm.)

For tuning of the PDMS´ elastic modulus and thermal conductivity, the liquid alloy is mixed in as isolated droplets in the PDMS matrix. The liquid fillers can tune mechanical and thermal properties with a large variation. The capillary behavior of the PDMS can keep liquid fillers inside the matrix both during mixing and after curing. The PDMS matrix can isolate the liquid alloy fillers without leakage under dynamic deformation within a certain stress level.

As a proposed model, a geometric mean model was matched in the low volume fraction range but high volume fraction conditions with inclusion interaction need another theoretical model, such as the liquid inclusion theory. The Eshelby´s inclusion theory (or Mori-Tanaka equation) may explain the liquid effect on the stiffness change of an elastomer in the liquid alloy-PDMS system.[114,197] If the interface between a matrix and spherical fillers is perfect without any interfacial debonding (dewetting), the Mori-Tanaka equation can be described as

$$K = K^{\mathrm{m}} + \frac{f(K^p - K^m)}{1+(1-f)\frac{K^p - K^m}{K^m + 4\mu^m/3}},$$

where K (Pa) is the bulk modulus of the composite, K^m (Pa) is the bulk modulus of the matrix, K^p (Pa) is the bulk modulus of the particle (filler), f is the volume fraction of particles (fillers), $\mu^m = E^m/2(1+\nu^m)$ (Pa) is the shear modulus of the matrix and ν^m is the Poisson´s ratio of the matrix. The relationship of the bulk modulus with tensile modulus and shear modulus is known as $\mathrm{K} = E/3(1-2\nu) = 2G(1+\nu)/3(1-2\nu)$, where G (Pa) is the shear modulus of the material.

Depending on liquid inclusion volume, the theory estimates the stiffness change of the composite. Liquid inclusion works as a softener in a medium. Recently, solid surface tension (capillary effect) of a soft solid surface in a

liquid inclusion system was found, which a liquid differently affects to the stiffness change of the polymer medium depending on the modulus of a soft medium in a liquid-soft silicone system.[114] In this thesis, a liquid alloy/PDMS composite was prepared, Figure 14. The droplet size, shape and distance between droplets defined by the filler fraction and processing can determine the property of the composite, such as tensile modulus and thermal conductivity.

Soft Thermal Contact

Thermal conductivity. Thermal conduction is defined by heat flux through a temperature gradient between two contacted media by Fourier´s law (1822). Phonon waves are scattered at disorders in a crystal structure. The phonon vibration is disturbed by the atomic structure, grain boundaries, imperfections, dislocations, interfaces of fillers, and randomness of the polymeric network. In a soft material, the thermal conductivity is reasonably low due to its disordered structure which disturbs phonon propagation.

Thermal diffusivity (m^2/s), α, is

$$\alpha = \frac{k}{\rho C_p},$$

where k (W/m·K) is the thermal conductivity, ρ (kg/m³) is the density and C_p (J/kg·K) is the specific heat capacity. (The Xenon flash method uses the relationship by calculating C_p of a sample by a comparison with a reference value.) The thermal conduction equation (Fourier equation) in a system is

$$Q = k(\frac{A}{L})\Delta T,$$

where A (m^2) is the cross-section area, L (m) is the length of the heat conduction and ΔT (°C) is the temperature difference at both ends through the medium..

Thermal contact resistance. A thermal contact between two surfaces resists heat transfer at the interface. Usually, the contact area between two surfaces is not perfect. Therefore, the thermal contact resistance is considerable in most cases, especially in thermal devices. A TIM is beneficial to thermal management in many systems, especially microelectronics, such as power electronics, high frequency transistors, or light emitting diodes. The relationship of the mechanical contact (pressure) and the thermal contact resistance was extensively modelled and experimentally characterized in the 1970s by Cooper, Mikic and Yovanovich, in order to design metal joints.[198-200]

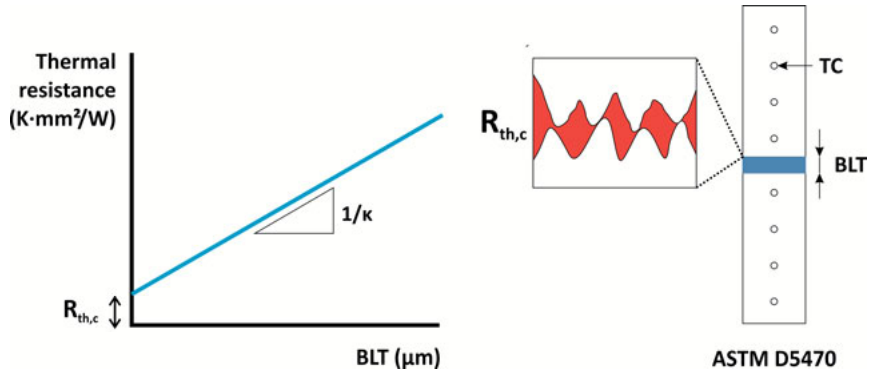

Figure 15. Thermal resistance vs. BLT by the ASTM-D5470 method.

Recently, nanomaterials are widely distributed in many research fields and thus, it becomes important to measure thermal contact resistance in the nanometer scale.[201-203] Based on phonon vibration and the Wiedemann-Frantz law, thermal conductivity and thermal contact resistance between heterogeneous layers are measured with an optical technique, such as the time-domain thermoreflectance (TDTR) technique by D. A. Cahill (Purdue University, USA)[204,205] and the Raman system by A. A. Balandin (University of California, Riverside, USA)[134,206]. The ASTM D-5470 method is a widely accepted method used to measure thermal contact resistance. Thermal contact resistance can be obtained for zero thickness by extrapolation of measured data from samples of different thickness. The thermal contact resistance can be defined as

$$R_{th} = 2R_{th,c} + \frac{t}{\kappa},$$

where R_{th} (K·mm^2/K) is the thermal resistance of the TIM sample, $R_{th,c}$ is the thermal contact resistance on both surfaces contacted with the measurement setup, t (μm) is the bond line thickness (BLT) and κ is the thermal conductivity of the thermal interface material, which is shown in Figure 15. Thermal conductivity and thermal contact resistance of the liquid alloy and TEC were characterized with the ASTM D-5470 method and the Xenon flash method in this thesis.[207]

Thermal conductivity of composites. For thermal conductivity estimation, the composite theory can be applied to calculate the effective thermal conductivity of a composite. Mainly, thermal conductivity is affected by orientation or alignment of filler materials. Phonon scattering is an essential point to control for the thermal conductivity at the interface between fillers and medium. With the spherical geometry of the liquid alloy, the geometric mean model of the rule of mixtures[208] can be applied to the TEC.

$$\kappa_{eff} = \kappa_f^{\varphi} \cdot \kappa_m^{(1-\varphi)},$$

where κ_{eff}, κ_f and κ_m are the thermal conductivity of the TEC, the filler and the polymer matrix, respectively, and ϕ is the volume fraction of the filler.

In this thesis, the TEC makes a tight contact to a rigid surface due to its compliance. The stretchability of the TEC could perform in a niche application under a dynamic environment. Compliant thermal microsystems need the TEC to have a higher efficiency when they become more sophisticated in the near future.

Stretchable Elastomer Network

Elastomer modulus and stretchability. Most polymers are viscoelastic. This is especially true for polymer (gel) that demonstrates both of a liquid-like and of a solid-like behavior. In polymer science, mechanical properties are largely governed by macromolecular structures, such as cross-linking network structures, molecular weight and chain alignment. Elastomers are amorphous, usually cross-linked network polymers above its glass transition temperature. The mechanical properties of cross-linked elastomer can be described using the rubber elasticity theory. A cross-linked elastomer can be reversibly stretched and released by thermodynamically storing the strain energy in the cross-linked networks. The entropy of cross-linked and entangled chains becomes lower when stretched. The elastic modulus (compliance or stiffness), toughness, relaxation (hysteresis) and stretchability of an elastomer are governed by its cross-link network structure and entanglement morphology.

An elastomer has a nonlinear stress-strain behavior and hysteresis by rearrangement of polymer chains induced by strain. From the thermodynamic model, the retractive force is related to entropy but not engaged with enthalpy change. The applied external force equals the sum of an energetic contribution, f_E, and an entropic contribution, f_s. In a rubber, the entropic contributions are dominant over the energetic contribution. An ideal network has no energetic contribution. The retractive force can be defined as

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

where f_E is the energetic term related to the change of internal energy by dimension change of the elastomer, f_S is the entropic term related to temperature and entropy change by dimension change of the elastomer, U is the internal energy of the elastomer, f is the external force applied to the elasto-

mer, L is the length of the elastomer, T is the temperature of the elastomer, and V is the volume of the elastomer.

Cross-linking network and liquid inclusion. The elastic (tensile, shear and bulk) modulus and stretchability of an elastomer are highly related to the density of cross-linking (chemical cross-linking by covalent bonds). The stretchability (elongation at break) is related to cross-linking and entanglement (physical cross-linking) density. For instance, heterogeneously cross-linked networks including loosely cross-linked or uncross-linked domains act as liquid-like inclusions in the network, Figure 16.[110] Heterogeneity gives an elevated softness and stretchability, which allows extended strain.

The amount of liquid-like inclusions, such as free polymers or heterogeneously cross-linked network domains, can be estimated with sol extraction from a gel network. To verify a cross-linking network, a swelling ratio, S_r, can be determined by allowing the net-polymer to swell to equilibrium in a good solvent for the polymer.

$$S_r = \frac{Weight\ of\ swollen\ polymer}{Weight\ of\ original\ polymer}$$

The swelling ratio can be compared with a reference sample and the cross-linking molecular weight can be calculated with the Flory-Rehner equation and used for estimation of the cross-linking network structure. The relationship between the equilibrium swelling and the degree of cross-linking by the equation is described as

$$-[ln(1-\nu_2)+\nu_2+\chi\nu_2^2] = nV1\left(\nu_2{}^{1/3}-\frac{\nu_2}{2}\right),$$

where n is the number of network chain segments bounded at both ends by cross-links, $n = \frac{1}{\nu M_c}\left(1-\frac{2}{M_c}\right)$, ν is the specific volume of the polymer, M_c is the chain molar mass of the network, ν_2 is the volume fraction of the polymer in the swollen mass, $\nu_2 = \frac{\omega_1/\rho_1}{\omega_1/\rho_1-(\omega_2/\rho_2)}$, ω is the weight of the polymer or solvent (subscript 1and 2 denote a polymer and a solvent, respectively), ρ is the density of the polymer or solvent, V is the molar volume of the solvent, $V = \frac{M}{\rho}$, and M is the molecular weight of the primary molecule.[209-211]

PDMS can be swollen with a non-polar solvent, such as hexane or cyclohexane. The Flory solvent-polymer interaction parameter, χ of PDMS to cyclohexane is 0.48 at 25 °C.[212] The average molecular weight between crosslinks, M_c, is a parameter that informs about the degree of cross-linking.

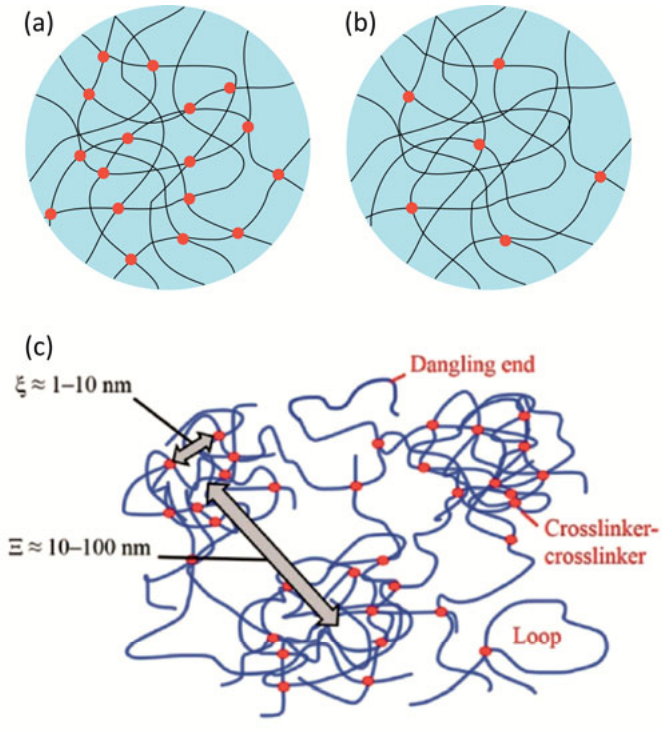

Figure 16. Network structures with cross-links and entanglements. Cross-linked networks of (a) a high density, (b) a low density and (c) a heterogeneous density. The red dots indicate cross-linking. The short arrow marks a typical mesh size, whereas the long arrow indicates the typical length scale of spatial variation of crosslinking density. (Figure (c) is reprinted with permission from ref.[110]. Copyright 2015 Royal Society of Chemistry)

When there are imperfections in a network such as free polymers, the relationship between the shear modulus and the average chain molecular weight is

$$G = \frac{\rho RT}{M_c}\left(1 - \frac{2M_c}{M}\right),$$

where R is the gas constant per mole, and T is the absolute temperature. When the primary molecular weight is sufficiently high ($1/M \rightarrow 0$), $G = \rho\, RT/M_c$. A typical swollen PDMS with cyclohexane is shown in Figure 17.

The gel fraction, G_f, can be obtained by extraction using a solvent for the polymer to wash out all non-crosslinked components (the sol fraction) leaving the gel fraction being the cross-linked fraction of the network.

$$G_f = \frac{Weight\ of\ deswollen\ and\ dried\ polymer}{Weight\ of\ original\ polymer}$$

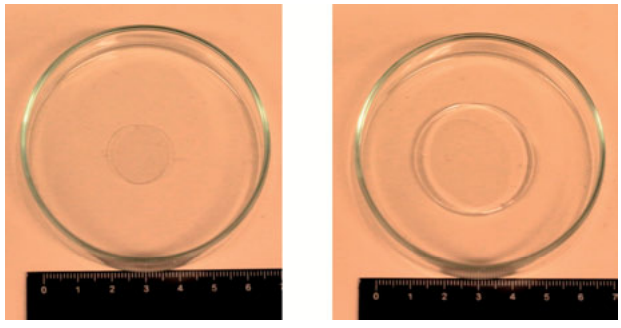

Figure 17. A PDMS piece (left) and its swollen state (right).

In this thesis, PEIE is introduced to the PDMS prepolymer to tune the mechanical properties of the cross-linked elastomer. The changed cross-linking network structure was investigated with test of degree of swelling, sol extraction to give measurable parameters for the Flory-Rehner equation. Network characterization together with performance test demonstrated that liquid-like heterogeneity inclusions with loosely cross-linked networks are efficiently tuning the mechanical properties for compliant microsystems which are soft, deformable and stretchable.

Soft Surface Adhesion

The adhesion mechanism originates from many different interactions. After J. D. van der Waals (Nobel laureate in physics, 1910), the adhesion force was much better understood and could be utilized in real situations. In the van der Waals interaction a contact surface area is a principal parameter of adhesion strength. Atomic attraction forces between two surfaces in the nanometer scale make the van der Waals force effective, which mainly originates from dipole interactions at physical contact. Interaction forces between permanent dipoles (Keesom interaction), between permanent dipoles and induced dipoles (Debye interaction) and between induced dipoles (London dispersion interaction) contribute to the van der Waals force (~10 kJ/mol). Hydrogen bonding (~21 kJ/mol) is caused by electrostatic forces, mainly between hydrogen associated electronegative atoms (-F, -O, -N) and neighboring electronegative atoms. Electrostatic forces (~15 kJ/mol) occur between charged surfaces. Mechanical interlocking of free dangling chains of a polymer to another surface can result in stickiness. Electrostatic forces by surface charging are strong adhesion forces. Liquid wetting or a capillary force also works as an adhesion force. Schematics of several adhesion forces are depicted in Figure 18.

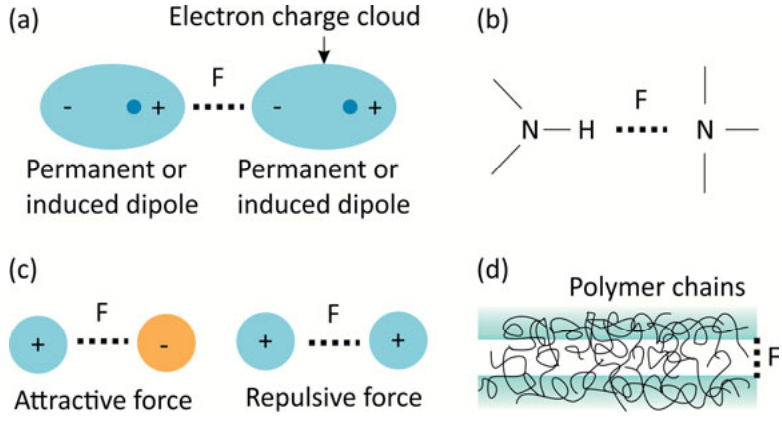

Figure 18. Schematic drawing of adhesion principles. (a) van der Waals interaction, (b) hydrogen bonding, (c) electrostatic interaction and (d) polymer chain dangling end interlocking.

In this thesis, the S3-PDMS is self-adhesive, possibly due to van der Waals interaction and free polymer dangling ends. Wetting and spreading due to high compliance and stretchability assist the surface contact. Stress distribution around adhered contact points can improve adhesion due to the low modulus and stretchability.

Soft Material Processing

Liquid Alloy Patterning

Contact type printing with a shadow mask is a well-known technique for large area patterning. Depending on mask resolution and liquid material properties such as wetting and viscosity, printing process conditions vary. For a simple processing, a tape mask was prepared with a cutting plotter. Transferring the tape mask via a transfer tape from a liner to a PDMS surface was used to keep all sophisticated patterns on the tape mask. In addition, a metal stencil mask or photoresistor mask was employed to alter the tape mask. Printing of the liquid alloy on a semi-cured PDMS surface is done by a paint roller. The wetting of each surface should be controlled, including a roller head, mask and the PDMS surface. Hence, materials and surface structure need to be selected to matching well with each other. A spraying process as one of the printing techniques is adoptable to liquid alloy patterning due to the liquid status and low viscosity. The ejected liquid alloy droplets from the spray nozzle by pressurized gas can have high momentum due to the high density of the liquid alloy and the high speed. The nanometer size liquid alloy droplets can be merged together when they collide. The spraying process worked for many different surfaces apart from the Teflon surface. Both types of printing methods, rolling and spraying, are useful for large area fabrication, but the non-contact type spraying technique resulted in better pattern quality, Figure 19.

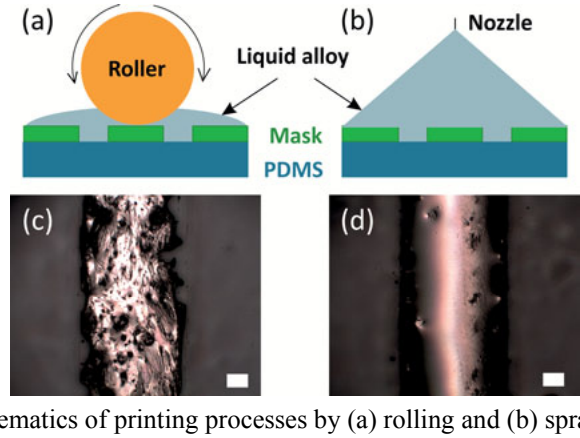

Figure 19. Schematics of printing processes by (a) rolling and (b) spraying and the patterns from (c, d) the respective technique. (The scale bar indicates 100 μm.)

Mechanical Property Tuning of PDMS

Engineering a polymer network structure can tune mechanical properties such as elastic modulus and stretchability. Microstructures of a polymer network; cross-linking, entanglement, chain orientation or alignment, chain linearity, chain length and its homo-/heterogeneity can be associated with the properties of the polymer. Polymer processes including die-casting, injection molding, spinning, extrusion, mechanical mixing, layer-by-layer coating, electric or mechanical stress field-applied processes can affect to the polymer network structure as well.

A composite with an additive filler, blend with a polymer, chain alignment control in an external field, interpenetrating network with separately cross-linked networks, bottle-brush functionalized chains, metal-organic framework are possible approaches to tune polymer properties.

In this thesis, the liquid alloy is introduced to PDMS, which results in the TEC (Figure 20 (a) and (c)) and PEIE being mixed with PDMS, which results in the S3-PDMS (Figure 20 (b) and (d)). In the silicone elastomer, the mixing process, such as mixing speed, time and vacuuming can influence the network structures. The curing conditions, such as time and temperature are critical to form a cross-linking network structure and reaction with additives. The TEC was obtained by high speed mixing for having small size droplets from tens of nanometer to a few micrometers in the diameter. The percolation threshold for electrical conductivity was 95 wt% of the liquid alloy and the mixture cannot be cured. The S3-PDMS was prepared with low speed mixing but high speed mixing or long storage made a better diffusion of PEIE in PDMS, which led a longer curing time.

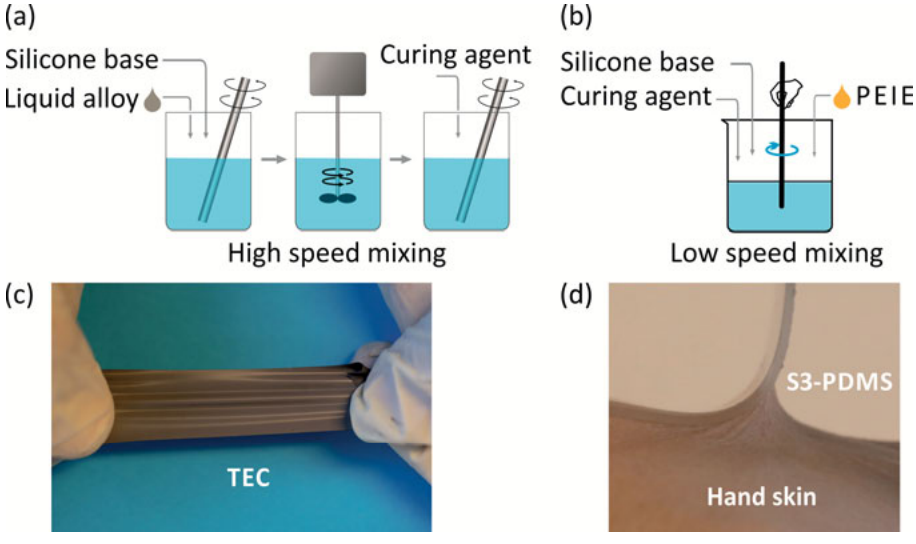

Figure 20. Material processing for (a) a TEC and (b) an S3-PDMS, (c) the fabricated sample of (c) the TEC and (d) the S3-PDMS.

Compliant Microsystems

Compliant microsystems can give conformality, stretchability, lightweight and large area implementation. Soft materials and processing methods were considered for compliant device designs. Properties of soft materials should meet the requirement of device performance, such as geometrical dimension, elastic modulus, maximum stretchability, temperature range and implementation. Processing methods need to be properly combined with selected soft materials by considering processability to minimize the number of trials and errors in the fabrication steps.

Many liquid alloy-based proof-of-concept devices have been demonstrated, for instance a strain sensor, pressure sensor, actuator, WPT coil, antenna, organic transistor and memristor, etc. Here, liquid alloy patterning and elastomer structuring are taken into consideration to make soft and stretchable devices such as a strain sensor, a thermoelectric generator as well as wireless communication applications, by following a classical theory of the solid devices. For fabrication of a device, hybrid integration with heterogeneous components and layer-by-layer structuring for a multilayer or 3D structure were employed together with liquid patterning and multi-functional packaging materials that were developed. Millimeter scale devices that have micro scale structures were made to take advantage of the liquid alloy conductor, which has high electrical conductivity and excellent processability of large area fabrication compared to a submillimeter device. Fabricated devices were tested in a stretching setup under dynamic conditions.

Stretchable Strain Sensor

A stretchable strain sensor is the solution for a large-stroke strain measurement, which is enabled by a combination of the liquid alloy and the silicone elastomer. This is the only materials that can realize such a long deformation measurement, which is made with metallic and liquid property of the liquid alloy. The strain sensor works with resistance change of a resistor which has long resistor pattern in the strain direction to increase resistance change.

The resistance is defined as $R = \rho\, l/A$, where ρ (Ω·m) is the resistivity of the resistor material, l (m) is the length and A (m^2) is the cross-section area of the resistor. A gauge factor (GF), representing the sensitivity by a ratio of the conductor´s resistance change to an applied strain, can be calculated as

$$GF = \frac{\Delta R/R}{\epsilon},$$

where R (Ω) is the resistance of the liquid alloy resistor, ΔR is the resistance change by strain and ε is the strain applied to the strain sensor.

For a better design, mechanical aspects of the sensor device can be considered, such a tensile modulus, compressibility, maximum stretchability and bonding strength of interconnects to the elastomer packaging. For example, the modulus of a packaging material should be lower than that of the target surface. Implementation of the sensor is another issue and the S3-PDMS can be a good solution due to its strong self-adhesion.

Depending on the strain direction, a resistor pattern can be designed to have a high sensitivity and a low Poisson´s ratio material will help to improve the GF to increase the resistance change inside the channel. The sensor pattern can be used as a temperature sensor and a heater as well. The fabricated strain sensor with a liquid alloy resistor and the S3-PDMS is attached on skin, Figure 21.

The printing-based large area fabrication technique can pattern a long connected line or many small patterns on the same plane at the same batch, while the injection technique cannot fill in unless a channel has many inlets and outlets. For a small size sensor, a high resolution patterning technique is required, which can increase the potential to design a small size dynamic system.

The performance of the stretchable strain sensor is reliable at different frequencies and many cyclic situations. It showed the same resistance curve after 1,000 cycles. Inertia effects of the liquid alloy flowing in a device may possibly reveal an unexpected effect in high frequency performance. Interconnectors for instrumentation are the weak points in real use. Stiffness gradient around the interface of heterogeneous stiffness materials is useful in assembly. A dedicated interconnect will be beneficial to interface between the strain sensor and hard cables. Otherwise, wireless communication can give a solution with better mobility.

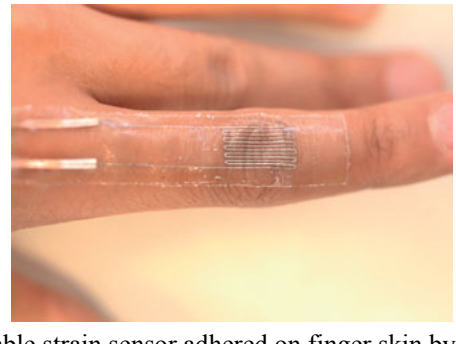

Figure 21. A stretchable strain sensor adhered on finger skin by the self-adhesive S3-PDMS.

Compliant Thermoelectric Generator

Thermoelectrics (TE) can be described by the Seebeck effect and the Peltier effect at the junctions of heterogeneous materials, and by the Thomson effect in materials. Thermal energy can generate an electromotive voltage by excitation of the electrons. Usually, three effects exist with combination of Joule heating when there is a temperature gradient or an electric current in a circuit. The Seebeck coefficient represents the ability to generate an electromotive force by a temperature gradient at the junction of two different conductors found by T. J. Seebeck (1821). The Seebeck effect is described as

$$V = S(T_h - T_c) \ ,$$

where V (V) is the electric potential difference, S (V/K) is the Seebeck coefficient, T_h (K) is the temperature of the hot side and T_c (K) is the temperature of the cold side in the circuit. For low temperature applications below 200 °C, bismuth telluride[213-215] doped as n-type and p-type shows high Seebeck voltage. In the thermoelectric generator (TEG) structure, p- and n-type thermoelectric legs were connected in series to increase the generated voltage. For a high efficiency system, high electrical conductivity and low thermal conductivity of the TE materials are required. On the other hand, both high thermal conductivity and high electrical conductivity of the contacts at the junction help to increase power generation by decreasing resistance. Contact resistance is an important issue for efficiency and reliability.[216-219] Conventional products have a problem at the junction due to metal diffusion of the solder into the TE legs, inducing a property change, and solder melting, resulting in hot spots at the junction. A packaging material needs high thermal conductivity and electrical insulation.

For a stretchable thermoelectric generator (STEG) design, the liquid alloy enables stretchable performance that is not delaminated from mechanical strain. The liquid alloy interconnect compensates and moderates the mechanical mismatch between the TE legs and the packaging material surface. The design of an STEG is the same as a conventional TEG and the fabricated STEG is shown in different packaging, Figure 22.

To reach a high ZT (figure of merit) of the device, thermal conductivity, electrical conductivity and the Seebeck coefficient of the TE materials are considered together with a contact resistance. The figure of merit is

$$ZT = \frac{S^2 \sigma T}{\kappa} \ ,$$

where σ is the electrical conductivity and κ is the thermal conductivity of TE materials. The efficiency of the STEG is expressed by

$$\eta = \frac{\Delta T}{T_h} \times \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+{}^{T_c}/_{T_h}},$$

where η is the efficiency of the STEG, ΔT (°C) is the temperature difference through the TE structure, T_h (°C) is the temperature of the hot side, T_c (°C) is the temperature of the cold side and ZT is the figure of merit.

Due to the high thermal resistivity of the packaging material, a silicone elastomer which is thermally insulating, the power efficiency of an STEG needs to be increased. One possible solution is using the thermal elastomer composite (TEC) as the packaging material which gives an efficiency increase close to 1.8 times compared to the PDMS packaged one. This is a similar level of increase as for the corresponding thermal conductivity increase of the TEC.

Thermoelectric power generation accompanies the Peltier effect and Joule heating during operation. To reduce losses from these effects, the thermal conductivity and electrical conductivity at the junctions between TE legs and interconnect should be as low as possible. The total energy in the TE structure is the sum of the Seebeck power, Peltier effect and Joule heating.

$$Q = IST - \kappa\Delta T - \frac{1}{2}I^2R,$$

where Q (J) is the total energy, I (A) is the current through TE structure and R (Ω) is the resistance of the TE material and contact resistance. When TEG generates more electric current, the Peltier effect and Joule heating are increased. Therefore, the electrical resistance of TE materials and the contact resistance between TE materials and liquid alloy interconnect is the point to be improved.

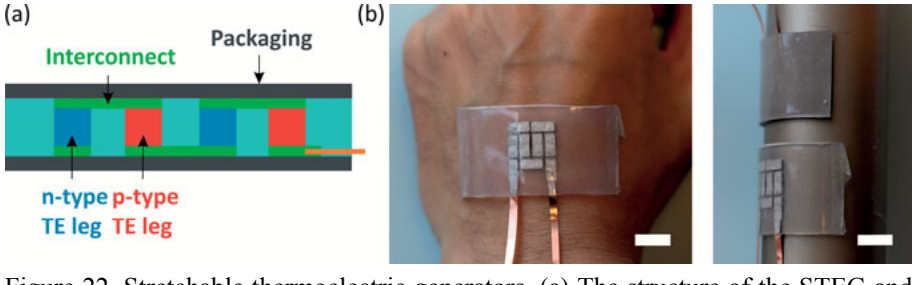

Figure 22. Stretchable thermoelectric generators. (a) The structure of the STEG and (b) the fabricated STEG on a hand and pipe. (The scale bar indicates 10 mm.)

Deformable Wireless Systems

A stretchable wireless component, such as an antenna or coil, can be useful for autonomous compliant microsystems. The liquid alloy works for high frequency applications due to high electrical conductivity. Stretchable shape can show tunable performance by shifting resonant frequency and bandwidth.

For a stretchable inductive coupling coil, the Q factor, coupling factor (k factor) and impedance matching needed to be designed and optimized to give high efficiency. The inductance, capacitance and resistance were semi-optimized in a coil design (size, distance between turns and core assembly) with circuitry impedance. The dielectric permittivity of the silicone elastomer affected system efficiency. The TEC had a low dielectric loss at high frequency above the GHz range.

The Q factor indirectly shows the system efficiency, which is the ratio of stored energy to energy loss in an oscillating system. Usually, a Q factor in inductive coupling systems of around 100 is useful. The Q factor is related to the coil design, which is defined as $Q=\omega L/R$, where ω is the angular frequency ($\omega=2\pi f$), L is the inductance and R is the resistance of the coil.

The coupling factor, k factor, in this case for electromagnetic wave coupling through two coils, represents how the electromagnetic flux can transfer from a transmitting coil to a receiving coil, Figure 23. The coupling factor is related to relative positions of each coil; distance, angle and alignment. A magnetic core can improve the coupling factor. The k factor is defined as

$$k = \frac{L_{12}}{\sqrt{L_{11} \cdot L_{22}}},$$

where L_{12} is the coupling inductance, L_{11} and L_{22} are the self-inductance values of the coils. All these devices can be related to changes of properties of the constituent materials in the device under strain conditions and a liquid alloy conductor and functional elastomers can adapt to any dynamically extreme environment. The fabricated stretchable WPT system is shown in Figure 23.

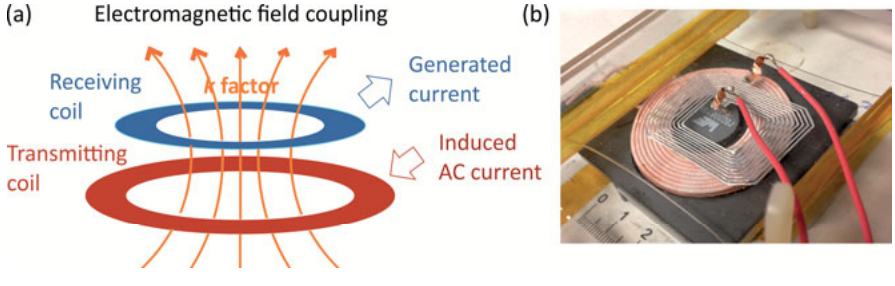

Figure 23. A wireless power transfer system. (a) Schematic drawing and (b) the fabricated stretchable WPT system.

Characterizations of Soft Materials and Devices

Material and Pattern Characterizations

Scanning electron microscope. The electron wavelength permits observing a microstructure down to 0.4 nm (SU9000, Hitachi) depending on sample surface property. A polymer sample was coated a Pd thin film by sputtering. Microstructures of samples including a liquid alloy pattern, TEC and S3-PDMS were observed by field emission scanning electron microscopy (FE-SEM, Leo 1550, Zeiss).

Optical profiler. An optical profiler (NT1100, WYKO) works with interference of reflected light from a reference and a sample. The optical profiler can measure the topology of a liquid alloy pattern without physical contact. The VSI (Vertical Shift Interference) mode can measure with a resolution of 3 nm. The optical profiler is one of the instruments that can measure liquid alloy pattern thickness.

Optical microscope. An optical microscope is the most basic instrument but also a most important instrument for scientific research. To analyze processing, patterns and sample, an optical microscope is necessary. An optical microscope may be used for thickness measurement by focal depth control but repeatability is not acceptable.

Xenon flash machine. The Xenon flash method (Nano flash, Netzsch) was chosen for thermal conductivity measurement of the TEC. Low thermal conductivity measurement needs a reference sample that has a similar thermal conductivity level and the same shape. Sample preparation with graphite coating is influential to the measurement to get reliable data. The specific heat capacity was measured with differential scanning calorimetry (DSC) but the data varied without consistency for the TEC sample. Density was measured with a density measurement kit for Xenon flash measurement, which works on the Archimedes principle. Thermal conductivity and thermal contact resistance of the TEC were measured with the Xenon flash method.

ASTM D5470 setup. Thermal contact resistance of the liquid alloy and the TEC were measured with an ASTM D5470 setup. The sample was made to the same size as the device under test (DUT) and the measured value was compared with a reference sample (an SAC alloy, Sn-Ag-Cu alloy).

Universal tensile test machine. A tensile modulus was measured with tensile test machines (AGS-X, Shimadzu and Microtester 5548, Instron). Tensile modulus and cyclic performance of the TEC and the S3-PDMS were tested. The sample was prepared with a dog bone shape by cutting with a scalpel under a hard mask but it gave a variation. Therefore, a dog bone shape punching cutter was necessary to reduce the variation in the sample cutting, especially for an elongation at break test. The mounting of the soft samples can influence the measurement because part of the sample was squeezed and slipped out during the measurement. PDMS pieces were used to hold the sample at the mounting position to prevent a stress concentration and slipping.

Rheometer. The shear modulus of the S3-PDMS was measured with a rheometer (AR 2000, AT instrument). Samples with different conditions were prepared with the same size and geometry (parallel plate geometry). The samples were prepared with a punching cutter. The sample height was maintained during the measurement. With consideration of a linear modulus region of PDMS, the shear rate of 0.5 rad/s was used.

Thermogravimetric analyzer (TGA) instrument. Thermal stability and boiling temperature of the TEC and the S3-PDMS were measured with TGA.

Spring gauge. A spring gauge (dynamometer) was used for adhesion force measurements of the S3.-PDMS on human skin. Speed and angle of peeling off was controlled by a dedicated setup. A different spring constant was used depending on the adhesion force range of the samples. The sample was prepared on a plastic film to prevent it from being stretched during the measurement and was made as a thin layer for the same reason.

Atomic force microscope (AFM). An AFM was used for measuring the adhesion force of the S3-PDMS with a Si tip. The S3-PDMS was too compliant and sticky to measure its elastic modulus.

Contact angle measurement setup. The contact angle and surface tension of the liquid alloy were measured. The oxide skin of the liquid alloy caused different wetting on the PDMS surface. The contact angle should be averaged with different droplets because the wetting angle and area were sensitive to the experimental conditions. The syringe-pumping speed and height were important to have a similar contact angle data.

Device Characterizations

Stretching setup. A strain control setup was prepared with a linear guide stage. Fixation geometries were made with anodized aluminum to prevent a reaction with the liquid alloy. It is important that the edge of the DUT (sample mounting part) is rounded to avoid sample breaking by stress concentration. The setup was controlled by software provided by the manufacturer. The maximum speed was 20 mm/s and it was programmable with speed, acceleration, strain and cycling numbers. The stretching setup is shown in Figure 24.

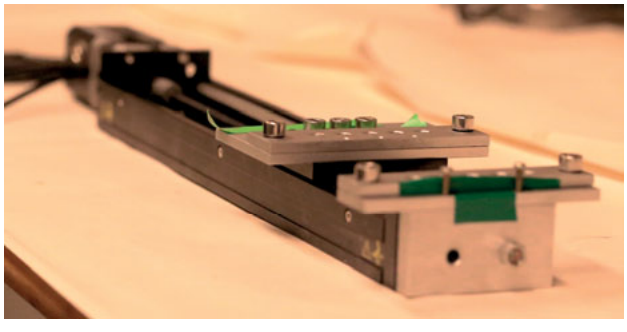

Figure 24. The automatic stretching setup for tensile strain and cycling.

Thermoelectric measurement setup. TE property and power measurement setup was built with Peltier elements controlled by a PID (Proportional-Integral-Derivative) loop of a Labview program. A hot and cold side can be robustly controlled and reached to a setting condition within a few minutes depending on the temperature range. Two power supplies that can change polarity for heat flux change of the Peltier elements allowed quick and robust temperature saturation. A sourcemeter was used for circuit impedance application to a STEG power measurement.

The set up can be heated up to 180 °C and cooled down to 10 °C due to the maximum temperature range of the Peltier elements. The addition of an external heating and cooling unit can increase the operation temperature range of the setup. The control accuracy of the temperature is 0.05 °C and the thermocouple (TC) tolerance was 0.5 °C. DUT areas made with copper blocks were 10 mm and 28 mm in diameter. A gold layer of 5 μm thickness was coated on the copper surface with electroplating to avoid oxidation of the copper surface and copper to gold diffusion was calculated to design the thickness of Au coating. Au has the same Seebeck coefficient with Cu. K-type TCs were inserted through the copper blocks and touched to the inner surface with thermal paste, which was close (500 μm) to the contact surface of the sample. The mounting pressure was controlled by a momentum controllable screwdriver. The established setup is shown in Figure 25.

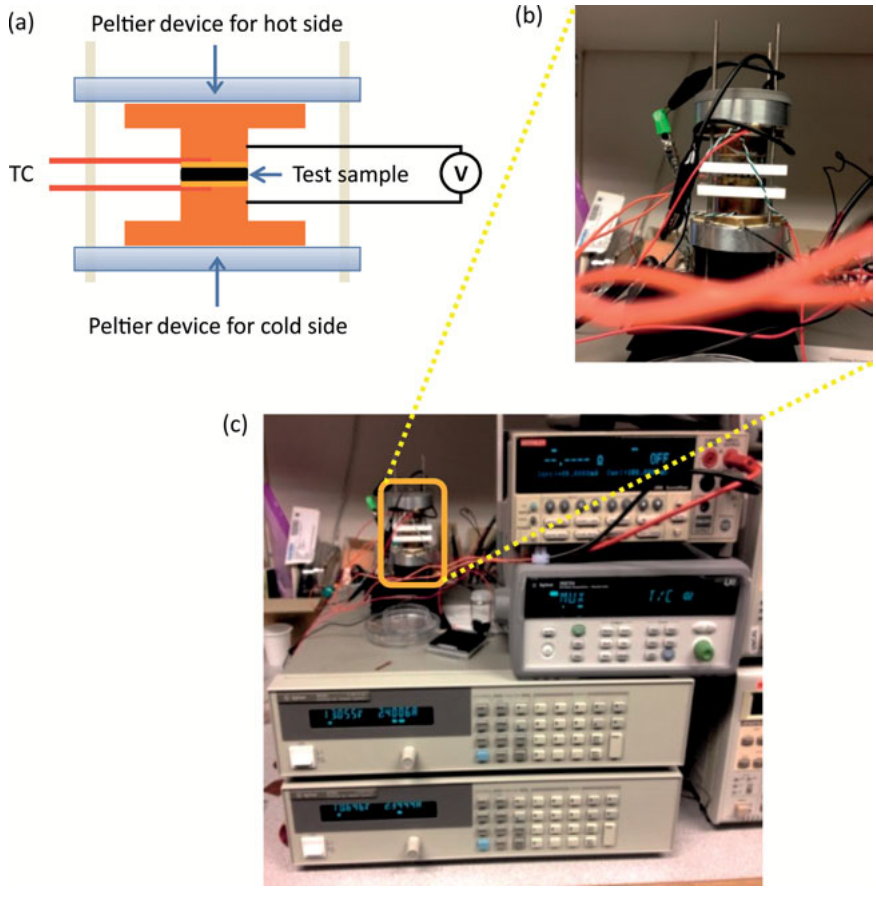

Figure 25. The thermoelectric measurement setup. (a) Schematics of the DUT and (b,c) photographs of the thermoelectric measurement setup.

Summary of Papers

Liquid Alloy Patterning (Papers I-IV)

For initiating the use of the liquid alloy in compliant microsystems, a practical patterning process was needed. Batch-type or continuous printing processes can promote large area and cost effective production. Printing base techniques were applicable for liquid alloy patterning.

Mask fabrication is an important process step for liquid alloy patterning. Metal and tape masks were employed as an easy and simple approach with a cutting plotter and chemical etching. Wetting of the liquid alloy on soft substrates through a mask was highly influential on pattern definition and connectivity. Liquid alloy patterns were analyzed in detail with an optical microscope, contact angle measurement setup, scanning electron microscope and optical profiler. Pattern analysis showed useful pattern quality.

Contact type printing was improved by employing spraying. Printing-based techniques with a shadow mask provided a 100 μm scale resolution due to mask fabrication process resolution. Currently, sub-100 μm patterns are developed by employing a dry film photoresistor and shrinking substrate. Controllability of resolution, thickness, oxide skin and wetting will extend the applications of the liquid alloy.

The tape mask can be used for a quick prototyping with design variations but a removal process of cut patterns should be improved for when a mask has many isolated parts. But for example, an antenna or coil design does not matter with this step because it has few connected patterns.

The liquid alloy has both metallic and liquid properties at the same time. There are several applications that can take advantage of this unique combination of properties; a stretchable strain sensor[220], stretchable energy device[221,222], stretchable antenna[223], cooling system[177,224-226], tribology[227], microfluidics[228-232], porosity measurement as well as soft electronics.

Achieving a higher resolution (< 1 μm) of liquid alloy patterning will be challenging. The oxide skin should be controlled by different means, such as oxygen and water vapor free environments or special gas environments. An automatic printing system for printing and spraying will definitely improve the patterning process reliability and pattern quality.

Thermal Elastomer Composite (Papers VI, VIII)

A stretchable form of thermal devices such as a temperature sensor, thermoelectric generator/cooler and high frequency radio frequency device need a thermal conductive elastomer for thermal management. High thermal conductivity of the thermal elastomer composite (TEC) will help to enhance device efficiency as well as an operation temperature range. Heat capacity is another parameter to be considered in a thermal device design.

We made a TEC, which is tunable in its thermal properties and mechanical stiffness. As a thermal conductor, a liquid alloy was embedded as liquid droplet fillers in PDMS medium. Thermal properties and mechanical properties were comprehensively characterized in different filler fractions and a thermal contact resistance was tested by the Xenon flash method.

The TEC at the highest concentration (92.5 wt% of liquid alloy fillers) that could be curable below 100 °C reaches 12-fold increase in thermal conductivity by keeping electrical insulating. Mechanical elasticity was maintained with 100% stretchability at the fraction. Characterization of the filler size distribution was challenging due to liquid droplet size ranging from hundreds of nanometer to a few micrometer. The control of the liquid filler size and shape can give an improved value in thermal conductivity and mechanical compliance. The interface between liquid fillers and an elastomer medium can be improved with a buffer material to make a better wetting or a diffusive bonding for a better condition of phonon propagation and stress distribution.

The TEC has good processability (flowing and casting) for microstructure fabrication, which comes from liquid fillers that have low viscosity and isolation of liquid droplet by a silicone medium. The sensitivity of a resistance temperature detector (RTD) and efficiency of a STEG were improved with the TEC. The thermal shape memory polymer shrunk more as well as faster on the TEC with a high volume fraction of liquid alloy fillers.

The TEC will be useful for the thermal interface of a dynamic strain condition for wearable electronics or soft robotics. In addition, the TEC may be useful for electromagnetic shielding or for stretchable telecommunication components with a tuned dielectric property for a high frequency antenna.

The liquid alloy oxide skin may give phonon scattering[233] at the interface, hindering thermal conductance. A well-made core-shell structure of the liquid alloy structure may give a chance to further improve the thermal conductivity and mechanical compliance. The dynamics of the thermal properties is interesting to be worth to further investigate.

Soft, Stretchable and Sticky PDMS (Papers VII)

To make use of the advantages of soft materials, mechanical property tuning enables more options to design compliant microsystems. For example, an elastomer softer than human skin (epidermis, elastic modulus lower than 1 MPa) is required for skin electronics. Modulus, stretchability, Poisson´s ratio and hysteresis can be the parameters that need to be tuned. By using an approach of elastomer network engineering, cross-linking and entanglement can be changed by blending with additives. Heterogeneous crosslink network structures can give a change of mechanical modulus and stretchability.

Here, we made an S3-PDMS with a tiny amount of a PEIE additive. Tuned mechanical properties were characterized both with a tensile test and with a rheology test. Several tests, for example, swelling test, sol-gel characterization, TGA and oven drying, were conducted to understand the polymer network structure. The adhesion force was measured with an AFM, spring gauge and load cell. The S3-PMDS was demonstrated with a self-adhesive strain sensor with a thickness dimension of a millimeter.

We obtained a S3-PDMS that was multi-functional and suitable for soft and stretchable devices. The processability (fluidity, bubble evacuating, casting and bonding) of the S3-PDMS was similar to that of PDMS (Sylgard®184, Elastosil®RT601) or EcoFlex®00-30. The adhesion on a glass mold was problematic when taken out from the mold. Softness (compliance) and stretchability come from the liquid-like, heterogeneous cross-linking network structure, which is either locally uncross-linked or loosely cross-linked. The adhesion force can be enhanced by intimate contact from a low elastic modulus and thus, a higher van der Waals interaction. Polymeric dangling ends, which are included as liquid-like polymers, assist the adhesion force. Stress relaxation at the interface due to the low modulus and stretchability helps the adhesion as well. The balance of the adhesion force, compliance and stretchability according to device geometry (thickness and adhesion area) can guarantee reliable implementation of a stretchable device against delamination when highly bent.

The S3-PDMS has a good potential for skin electronics or soft robotics. A self-adhesive surface can be useful in practical applications because a soft and stretchable packaging surface does not need an extra adhesive layer. Under dynamic deformation of a contact surface, low modulus and stretchability are mandatory so as not to disturb its dynamics. Elastomer structure control with liquid inclusions can give a chance to develop a compliant component, for instance, membranes for biological applications. Investigating the switchable adhesion force can be a next project and a stimuli-responsive elastomer by mechanical, thermal, electric, magnetic optical or chemical (pH, solvent swelling, ionic) fields are interesting to envisage “active”, soft and stretchable components.

Liquid Alloy Interface (Papers VI, VIII)

Integration of heterogeneous materials results in a physical contact, which unexpectedly has a large uncontacted area due to microscale roughness even though between shiny metal surfaces. The interface is always related to carrier transport of particles or waves in electronics or electrochemical systems as well as thermal systems. Compliant contact that can adapt to a surface roughness is the potential way to increase the contact area. For an interface under dynamic strain, soft and stretchable interface material is essential to reliable use.

A liquid or polymer can improve the contact with the conformal wetting. Surface conditions for wetting control are important for the wetting perfection. As a possible solution, the liquid alloy can provide a metallic contact or interface with liquid wetting. The liquid alloy interface can handle mechanical, thermal and electrical issues under dynamic strain conditions. Heterogeneous rigidity component integration survives with liquid contact that can allow slipping under stretch and release. Thermal and electrical contact can be maintained during mechanical vibrations or deformation by liquid adaptation. Mechanical stability and reliability have been proved from considerable times of device evaluations with stretch cycling. Thermal and electrical contact resistance were measured for certain combinations, *e.g.*, with a semiconducting Bi_2Te_3 surface by the ASTM D-5470 method and the four probe measurement method, respectively.

A reliable contact with a liquid alloy at the interface was achieved and it could be robustly realized with a developed liquid alloy spraying method. It was remarkable progress to have good wetting on most of the surfaces. An oxide-free liquid alloy interface has the potential of being used in liquid alloy-based microfluidic circuits and liquid cooling components. With a better understanding the wetting of the liquid alloy or polymers to different solid surfaces, mechanically dynamic, compliant systems can be designed in a better way.

Stretchable Sensors (Papers VI, VII)

Strain sensor. A liquid alloy-based stretchable strain sensor introduces a new possibility of measuring a large stroke of dynamics. A liquid alloy resistor sustains severe and harsh conditions due to its liquid nature. It is freely deformable without stress. The sensor is useful for human body motion sensing, which is useful to design dynamic systems, such as bioengineering simulations or robot. The stretchable strain sensors can be fabricated with the developed liquid alloy patterning methods with different elastomer packaging. The batch type fabrication scheme is easily combined with a tape mask. The fabricated sensors were evaluated with a real time monitoring connection of a multimeter and a stretch setup.
Temperature sensor. A stretchable RTD is useful for measuring the temperature of a stretching object. In addition, it can be used as a heating unit. The liquid alloy resistor was patterned in the TEC packaging with the liquid alloy patterning process. The RTD was tested on a hot plate with K-type TCs.

The stretchable strain sensor had a good GF around 2.0 and it was affected by a Poisson´s ratio of a packaging material and pressurizing effect in an operation. At high frequency, fluctuation or inertia of the liquid alloy and elastomer packaging can affect to the signal.[234] But the sensitivity, repeatability and linearity made it feasible to be used in real situations. The stretchable strain sensor could measure over 100% strain with EcoFlex 00-30 packaging (depending on a packaging material and interconnectors) but was limited to about 60% stretchability with PDMS when heterogeneous components were integrated. This is due to the increased stress concentration around a rigid component, such as a wire or electronic chip. Local stiffness cell (LSC), interface gradient or even fully soft material integrated systems can be solutions to increase the stretchability of a sensor. Otherwise, as a packaging material, a stretchable material that has a high toughness is required. Another liquid can be used for a strain sensor such as ionic liquid or electrolyte.[235,236]

The stretchable strain sensor could be applied to a rehabilitation system or a sports system for monitoring dynamics of a human body in the near future. This compliant, sensory motor feedback system like human skin is a promising building block for biomimetic systems.

The temperature coefficient of the liquid alloy was measured to be 0.0022 Ω/Ω/°C for the liquid alloy from room temperature to 100 °C. It had a combined effect of resistance changes from temperature variations and strains variation. From parametric evaluations with temperature and strain conditions, a diagram could be obtained with shifted resistance signal curves at different temperature conditions. Other types of liquid based temperature sensor have been reported as well.[237]

Thermoelectric Generator (Papers VI, VIII)

Harvesting waste heat from soft, uneven and dynamic surfaces is a unique solution for overcoming some limitations with a stationary and rigid, conventional TEG. For example, battery charging from human body energy can be a long-term project. A solar thermal system is a potential application for an STEG to generate electricity from the strong solar heating.

Bi_2Te_3 pellets (n-type and p-type) were integrated in an elastomer packaging via liquid alloy interconnects, which can make high efficiency at low temperature. Layer-by-layer processing with liquid alloy patterning and elastomer structuring were applied to fabricate multi-pairs of TE legs in series connection. The wetting of a liquid alloy on a Bi_2Te_3 surface was obtained with the spraying technique. Thermal and electrical contact between TE legs and liquid alloy interconnects are enough to work, and liquid alloy wetting stability is proved with thermal cycling. Diffusion of liquid alloy elements into TE elements may be an issue for a long term operation, especially at a high temperature range.

Liquid alloy interconnects were tested for thermal and electrical contact and thermal cycling was conducted to see affordability in a wide range of temperatures. The fabricated STEG were evaluated in the TE setup.

The STEG generates electricity at micro watt level at room temperature with 20 °C temperature difference. The liquid interconnects allowed deformation and stretching of the structure while keeping electrical contacts. The STEG can only be stretched up to 20% due to delamination of a Bi_2Te_3 leg from the packaging elastomer structure. Adhesion or bonding between soft and solid materials is a critical issue that needs to be improved. Many bonding methods have been tried but the best way is to use a sticky elastomer that is a low modulus and high stretchability. The TEC packaging improved output power by around a factor of two.

A thin TE structure with sputtering, electrochemical deposition or polymeric TE materials could provide a better geometry even though it has a lower efficiency.[238-240] When the contact resistance of the liquid alloy and thermal conductivity of the elastomer are improved, the TE structure can be useful as an active cooling unit of thermal actuation control, *e.g.*, for shape memory or phase change material-based systems. A TE liquid can be improved its electrical conductivity to be used a liquid TE system. [241]

Wireless Communication (Papers I, III-V)

To realize an autonomous compliant system that can be stand-alone to improve mobile, user experiences, a compliant and deformable wireless communication unit is necessary. Carrying wires in a soft and stretchable microsystem is a big burden due to 1) decreased mobility in a dynamic object movement, 2) a mechanical failure at the interface of wires surrounded by a soft elastomer and 3) an increasing complexity of a real application situation.

Stretchable RFID antennas with different designs were demonstrated with liquid alloy conductors. The readability of fabricated stretchable RFID antennas was tested with a transmitting coil under a stretching condition. A stretchable wireless power transfer coil was demonstrated with liquid alloy conductors. Coil design, impedance matching and positioning affect power efficiency. Stretching and positioning of the liquid alloy coil were examined and magnetic elastomer cores were prepared to enhance the coupling.

The stretchable RFID antenna showed a good readability under strain, compared to a reference antenna. It could be stretched up to 60% and was readable over a distance of 10 m. The resonant frequency of the stretchable RFID antenna was shifted towards a lower frequency by a larger strain. The intensity of the resonant peak was maintained with a small degradation.

The stretchable WPT coil worked at 140 kHz with 10% efficiency. It was comparable to a reference copper coil in the efficiency. Stretching of the coil was allowed for inductive coupling unless the alignment of the transmitting and receiving coil was shifted or the distance between them became longer. Stretchable magnetic cores, which were made with magnetic oxide nanoparticles or alloys in PDMS, helped to improve the efficiency, but the increases were small due to a low dielectric constant of the silicone elastomer medium. Different sizes of coil differ in power transfer efficiency and thus, impedance matching was necessary.

For realizing stand-alone wearable systems or mobile soft robots, compliant wireless communication and a WPT system can be beneficial. Wave disturbance or dissipation from surrounding objects needs to be considered in the design of a structure and materials. Higher dielectric elastomer packaging, such as the TEC, can give a useful gain of the form factor of an antenna. It can be adopted as a thermal triggering system or mechanical switch in wireless communication. Soft and stretchable characters can suggest a foldable antenna or size changeable wireless system. As a building block of compliant microsystems, wireless communication units can remove all wires from a device in a measurement instrument.

Concluding Remarks and Outlook

For compliant microsystems enabling the "soft technology", soft material patterning and structuring are studied in this thesis. *Liquid alloy patterning* and *multi-functional elastomers* are introduced to compliant microsystems that are soft and stretchable. Liquid integration in an elastomer can be a smart approach to make novel characters for compliant microsystems. Liquid alloy patterns on elastomers, and liquid alloy and liquid-like, heterogeneous matter inclusion in elastomer networks have been developed and characterized. For the related communities; microsystems, microfluidics, soft robotics, stretchable electronics and wearable electronics, simple and easy processing schemes are proposed for preparing multi-functional elastomers and for fabricating compliant microsystems.

The printing-based technologies for liquid patterning were easily adaptable to design changes, time- and cost-effectively. The 100 μm level resolution of liquid alloy patterns was achieved with tape mask transfer techniques. The spray method of the liquid alloy was robust on many different substrates. For further continuation of these ideas, higher resolution patterning and thickness control need to be developed for versatile and precise applications. Solidification (freezing) of liquid alloys and rolling of liquid alloys on a special architecture of VACNT arrays[242] have a room for being applied to a patterning process or an interface structure.

Tunability of mechanical properties of soft materials makes soft technology possible to fulfil practical requirements and to expand applicability in real life. The TEC and the S3-PDMS can be accommodated in thermally efficient and self-adhesive compliant microsystems. Liquid inclusion in soft materials provides an idea for tuning microstructures with a new processing condition and with other additives. Recently, theoretical work on liquid inclusion in soft materials has been understood by R. Styles *et al.*[98,114,194,195], which can be applicable to the TEC. Experimental approaches to investigate a heterogeneous network by S. Seiffert *et al.*[108-110,243] encourage further tuning of the network structure of the S3-PDMS. Soft materials can be engineered in a proper way by understanding the structures. Soft materials that have various functionalities, *e.g.*, modulus, elongation, thermal conductivity or permittivity, can lead to more useful and dedicated designs of an emerging system. Soft materials, which can be reconfigurable, reprogrammable and stiffness-changeable, are examples that should be sought for. For instance, soft robotics need multi-functional elastomers that can be assembled

with hard materials to build actuating parts that can touch a soft object. The jumping soft robot designed by N. W. Bartlett *et al*.[17] is a good example that has soft and hard materials together in the same system. The gradient in modulus made the highly powered jumping actuation possible.

Soft materials need smart processing technologies that can morph and shape soft materials in an effective and practical way and that can be commercially accessible as regards cost and time. Although the process technology for solid state materials may be adaptable to soft material processing, a printing-based approach for soft materials is the most proper methodology, such as 3D printing or additive manufacturing techniques. Soft and stretchable materials or structures that can change their shape or phase with external stimuli can provide new possibilities in soft material processing techniques, such as the 4D printing technique, recently demonstrated by A. S. Gladman *et al*.[244]

One missing element for a compliant microsystem in this thesis is a soft actuator that can move. A soft actuating material is in a huge demand for a soft robotic system. A liquid alloy actuator is demonstrated in an electrolyte with an electric field application by forming an electric double layer. A lab-chip device for carrying out drug delivery is proposed by Y.Lu *et al*.[166] Depending on the application, a stimulating method varies to actuate soft materials, such as an electric, thermal or mechanical field. For example, a soft actuating material, which can be stiffer under certain conditions by controllable stimuli and response, is highly in demand. A shape memory polymer and a liquid crystal elastomer have strong potentials to open this new venue. Controllable and reversible actuations by thermal energy, optical or magnetic fields are necessary for practical use, such as folding, bending or locomotion for a programmable, mobile compliant actuation system. Geometric design-driven actuation, such as origami, is a promising approach for a compliant smart system.

For designing such a material and system, there are plenty of designs in nature, which can be investigated to inspire soft technology. Bioinspired design mimicking mechanisms engaged in natural geometries in micro and macroscale can give smart solutions to make compliant smart systems. Natural designs can be applied to all aspects from a material level to a system level. Nature such as the human body or many other different biological systems, mainly consist of soft materials. More precisely, soft bodies are assembled with hard materials. Therefore, interfaces between soft materials and hard materials are important to mimic natural systems. As an example, a compliant sensory-motor system and soft man-machine interface, which mimic living organisms found in nature, will be the next step in future research.

For designing compliant microsystems, soft materials and processing techniques need to be comprehensively considered and properly hired and developed. From soft materials to compliant systems, multidisciplinary

knowledge including mechanics, viscoelasticity, dynamics, structural design, surface physics, composite, polymer science and processing techniques can be cooperative to develop novel ideas with different viewpoints. *Soft materials* and their *interfaces* are most important for the design of compliant systems in soft technology, and thereby "soft intelligence" will work in forthcoming soft and dynamic life.

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Svensk Sammanfattning

Vad händer om vårt liv styrs av en livlös och hård teknik? Människors liv har påverkats starkt av ny teknik som internet och smarta telefoner. Det kommer hela tiden och allt snabbare nya innovationer och de påverkar oss mer än någonsin tidigare. Vårt liv kommer antingen att styras av en hård och stel teknik eller så får vi styra den till att bli mjuk och följsam. Låt oss tänka noga efter vilken riktning vi vill att tekniken ska ta för att skapa en bättre framtid!

Vi står inför en stor utmaning med ett åldrande samhälle. Det blir mer äldre människor som behöver tas om hand och mindre unga människor som är produktiva. Förr eller senare kommer den höga medelåldern leda till att människors arbete allt mer behöver ersättas av tekniska lösningar och ett av de viktigaste områdena blir hur vi kan hjälpa det ökade antalet av allt äldre människor.

Hittills har mycket mänskligt arbete ersatts av maskiner som är starkare, snabbare och mer precisa än oss människor. Men för att ersätta många av de kvarvarande arbetsmomenten där maskiner idag inte kan ersätta mänskligt arbete behövs en mjuk och följsam teknik som erbjuder en beröring som liknar en människas. Ergonomiskt utformade, mjuka system som inte märks erbjuder även nya marknadsområden. En tydlig signal på intresset för den nya mjuka tekniken är att flera nya företag börjar erbjuda olika lösningar för detta: Softrobotics Inc. erbjuder mjuka robotfingrar monterade på en konventionell hård robothand för att skörda frukt eller grönsaker utan att skada deras ytor. MC10 Inc. har lanserat ett mjukt och följsamt plåster med olika sensorer och som trådlöst kan informera om olika hälsotillstånd. I framtiden kan de mycket väl kopplas till en automatisk läkemedelsdosering som dagens insulinpumpar. Ytterligare ett område som utvecklas snabbt är mjuka bärbara robotar, mjuka exoskelett, som kan erbjuda hjälpa vardagliga kroppsrörelser för sköra eller rörelsehindrade personer eller ge stöd vid tunga och krävande arbeten.

Hermann Staudinger fick Nobelpriset 1953 för sin för sina upptäckter inom makromolekylär kemi och då särskilt de polymera strukturerna. Sedan dess har polymerer kontinuerligt förändrat vår livsstil på många sätt som hur vi hanterar mat, tyg, konstruktionsmaterial för byggnader och fordon, engångsvaror, mediciner, med mera. Polymerer ger ofta fördelar i lätt vikt, flexibilitet, transparens och låg kostnad på grund av billiga material och enkel och snabb produktion. Den mest anmärkningsvärda fördelen är hur man

förhållandevis enkelt kan ändra dess materialegenskaper genom att ändra processförhållanden och genom att skapa kompositer. Vi är idag i en tid då polymerer övergår från att vara enbart passiva komponenter som konstruktionsmaterial till att bli aktiva komponenter. Ett exempel är aktiva polymerer i kontakt med en människokropp och då särskilt dynamiska system kopplade till människans rörelser. Här behöver funktionaliteten i dessa mjuka material vara anpassad till människans behov.

För mjuka och följsamma system behövs ett polymert system som är mycket mjukt och töjbart. De vanligaste är elastomerer. De gör det möjligt att skapa unika funktioner i mjuka system som en mjuk robot, biomedicinska verktyg på kroppen, och avancerade system som tillåter att man växer levande system som celler, konstgjord vävnad, muskler och organ. För att förverkliga olika väsentliga funktioner i mjuka system behöver man utveckla nya tillverkningstekniker för att strukturera mjuka material och använda olika tillsatser för att skapa kompositer och avstämbara materialegenskaper i dessa mjuka system. Det finns även elastomera hydrogeler som kan ge extra funktionalitet. Dessutom kommer miljö och hållbarhet att vara allt viktigare i materialvalet. Biologiskt nedbrytbara eller ätligt material kommer att ta en större i mjuka system.

I denna avhandling används två olika materialsystem, en flytande legering och en typ av gummi som kallas silikoner (eller kiselgummin, och ja, de används t.ex. för att täta med i våtutrymmen eller för bröstimplantat). Med dessa material har vi skapat nya mjuka och tänjbara system som kan användas som elektronik på huden eller till mjuka robotar.

Olika mönstringsprocesser har utvecklats för att kunna tillverka töjbara ledarbanor i mikroskala i mjuka och följsamma system. Här används den flytande legeringen som en mjuk och töjbar elektrisk och värmeledare (motstånd), en elektrisk ledare och som fyllmedel som blandas i silikonet. Mönstringstekniker baserade på mönstertryck har utvecklats för satsvis, parallell bearbetning av den flytande legeringen. Den bästa tekniken som utvecklades var en enkel och robust kombination av tryckning

Vi har använt silikon för att bygga mjuka och följsamma strukturer och som förpackningsmaterial. Därför har det utvecklats två olika sätt att variera materialegenskaperna hos silikonet. Ett sätt var att blanda i extremt små droppar av den flytande legeringen som fyllmedel i silikonet, så att det en mycket bättre värmeledningsförmåga. Det andra sättet var att göra ett silikon som passar att ha på huden genom att helt enkelt blanda in en polymer som lokalt binder den katalysator som annars härdar silikonet, så att det bildas som droppar av silikonolja i silikonet. På så sätt fick vi fram ett mjukt, töjbart silikon som fäster bra på huden utan att lämna rester när man tar bort det.

Det har även behövts ta fram nya sätt att karaktärisera såväl de nya materialen som de nya mjuka systemen och deras egenskaper. För att visa potentialen med dessa nya material och processtekniker har olika mjuka och

töjbara enheter konstruerats och tillverkats, som bl.a. en töjningssensor, RFID, trådlös effektöverföring, termisk energiskördare och antenner.

I vårt uppkopplade liv blir bra människa-maskin-gränssnitt allt viktigare för oss. Mjuka uppleverser, både fysiskt mjuka och bekväma och intellektuellt mjuka med intuitiv kommunikation, bör betraktas som bland det viktigaste som behövs för bättre livskvalitet och produktivitet i framtiden. För en mjuk dynamik mellan människa och maskin kan "mjuka maskiner" vara lättare att anpassa till oss eftersom människan till så stor del har olika mjuka egenskaper både fysiskt och mentalt. Mjuk teknik kan komma att ge oss ett unikt stöd i våra liv som inte vore möjligt med en hård och stel teknologi.

Self-Reflection

Living as an academic person, and especially working in the engineering side of it, is about endless learning and trying with curiosity on nature and human life. As a PhD student, this past period has been hard to be unhappy because there are a lot of interesting things around me. With my long experience from an industrial background, living with academic research at a university is one of my dreamful plans. It has been a graceful gift to me to allow for planning a new direction of my life. Moving from far away to Uppsala has been another adventure with my family. For making something new during my PhD research, I needed scientific knowledge from many disciplines that I have to remember or to learn. In the emerging field that I worked, such as stretchable electronics, soft robotics or compliant microsystems, it was not easy to dig out and to find out new ideas because the field is new with no baseline. Nonetheless, I loved, love and will continue to love doing it.

Compliant materials which give soft contact to surroundings (I would like to be like that in my personality.) have opened many possibilities in this era thanks to polymer technology. From material development to system integration, we can do many things that we cannot do without polymers. For a better human life, human engaged technology needs soft technology to make soft interface to help human life. Soft materials needs to be developed more and soft machines should be designed for a dedicated purpose, such a soft robotics or tissue engineering. Design ability for a novel system with understanding materials and processing techniques will be the key to open new areas and to attract common concerns.

Liquid alloy is a unique material that can arise many ideas for emerging applications. So far, many useful patterning techniques have been developed to make a working device. More understanding on the wetting and oxide skin will show new sides of its feasibility. Liquid inclusions in soft materials are highly interesting to me at this moment, for tuning material structure and properties as well as for making a liquid based compliant system. Liquid to soft interface and heterogeneous polymer network can be strongly related to make a compliant system in my understanding. I believe discussion and collaboration must be the only and best way to succeed in engineering research, especially in this field. A good team work can take care of most problems.

Now I would like to close my PhD page to try my written ideas that have not been tested in the lab for a while due to this thesis writing.

Acknowledgements

For PhD research, a wide range of learning with dirty and stupid trials to see how my ideas work have been done for the past four years. A lot of help from colleagues, professors, collaborators and communities made me better and helped me work well. I appreciate all your kind and beneficial help since the spring 2012.

First of all, I am grateful to Zhigang who has discussed a lot with me when we have new ideas and you guided me with care to allow me to find out my own way for research. I learned many things related to academia related things and a smart approach to do research. I know you trust me and wait for my trials with more patience than I deserve. Thank you! I also thank Zhibin as one of my supervisors, who always give a smile with discussion. I have done well with your kind help. We discussed how we can make the starting for the project work at the beginning of my PhD study. I also appreciate Shili who assisted me with strong supporting and I remember your lesson on how important equations are for research. I now totally agree with you, which will show up in my coming research. Klas, I would like to express to you my gratefulness for your friendly guidance and discussions with your strong positive energy. I got much help and cheering energy from you for PhD student life. I have been happy with you during all the discussions and talks. Thank you for all supervision.

Jöns, it is my honor to learn about silicones from you and thank you so much for your strong help in a short time. I like elastomers! I would like to make something with you more. .Kristofer, I appreciate your help for supporting experiments, discussions and friendly answers to my questions. I hope we can do the liquid inclusion project soon. Vassilios, thank you for your kind help in frequent experiments in the lab. Gunnar, thank you for your nice lectures and help with experiments. Hugo, I do not know how I can express my thanks for your assistance. Tusen Tack!

I have to say warm thanks for all the help from my colleagues in MST and FTE. Ville, I thank you for your gentle and nice talks and help in the many times when I asked tools and equipment. Stefan, I thank you for your help on MATLAB and Labview and of course for chatting with Victoria in many disputation parties. Javier, thank you for your hard working during your master study. Let´s do more together. Johan, thank you for your friendship and help for design circuits. I miss you. Lena, thank you for your help in many points. Andreas, thank you for your help for visualization. Greger,

thank you for your supporting of lab instruments. Pontus, I remember your help when I started my PhD study. Where are you now? Atena, thank you for sharing information around us. Maria, thank you for your supporting on lab related things. Bo, Peter, Kristofer, Martin, Martin, Anders, Gemma, Tao, Mingzhi, Frida, Mats, Sam, thank you for your help and kind chat.

Patrik, thank you for your collaboration and I hope you can finish your thesis writing well soon. Thank you. Malkom, thanks for your kind help with measurements. Mandy, thank you for your help for experiments. Indrek, thank you for giving your time to talk when I wanted to discuss about an actuator. Robin, I thank for your collaboration and I hope we can do something more soon. Uwe and Jörgen, thanks for your quick and valuable practical guidance in my experiment. Si, Shuyli, Zhiying, Darcy, thank you for your friendship with me.

I cannot mention every member of MST and FTE. Thank you, all! I cannot forget Jonatan, Sara, Per-Richard, Maria, Ylva and Ingrid. Thank you for your vital help to survive in my working place. Triobology MIM group, thank you for handy help. MSL, thank you for quick supporting in the clean room. Ångström workshop, thank you for your help to enable experiments.

Laurent, I appreciate you much for your kind help at Yverdon-Les-Bains during the hottest month in the year. I hope to see you again. Johan, I was glad whenever I worked in your laboratory and your students made me work harder because they were so nice. Thank you for supporting me in many characterizations and discussions. Yigit, I would like to express my gratitude for your kind recognition of my research at Livorno. I hope we can continue to discuss in our collaboration. Dickey, thank you for coming as my opponent. It is my honor. Voit, Melanie, thank you for your collaboration and provision materials and the process. Fredrik, thank you for your gentle help for the material test. Xavier, thank you for your collaboration. Christer, Leif, Tomas, Albert, thank you for your useful advises. Steven, I thank you for your strong support when I worked with you until midnight. Your help really worked for many cases. I was happy when I discussed with you about the measurement. Di, you had good influence on me. You have a really bright mind and I learned a lot from you. Magnus, thank you for your discussion on antenna, Jinxing, Umut, Bing, thank you for your supporting for material testing. Ana, thank you for your lesson of your material process, Fredrik, Mikael, thank you for your bright greetings all the time. Hu, thank you for your good AFM skills. Hauke, thank you for your help for the goniometer. Janne, Peter, thank you for your help for lab use. Wei-Tao, Alex, thank you for your friendship.

Soft robotics community, thank you for your kind welcome and arrangement of all meetings. Beneli, Swedishpharma, thank you for your kind answering for my asking for films and adhesives. Michael, Zhenishbek, Shintake, Seun, Sangwook, Wayne, thank you for your friendly discussions dur-

ing workshops. Frida, Albin, Arne, thank you for your nice teamwork with voluntary experimental elaboration.

Mikael and Malin, thank you for your friendship with me and my family. Your help and friendship have done my family well during my PhD study. Thank you. Anders, thank you for your essential help when I started my life in Sweden. Jungyul, thank you for your help and staying in Uppsala.

Most importantly, THANK YOU! My family, lovely wife, Chris and Jimin. You helped me a lot with your patient waiting and I appreciate your care for me. I am sorry that I have not given enough time to you. I love you with my true heart. I will do better. Thanks again. Tack, Chris och Jimin. And I always have a grateful mind to my parents and parents in law. Thank you for your understanding and your appreciation.

Finally, I truly appreciate the help by the funding for my PhD study including the faculty funding from the Department of Engineering Sciences, Swedish Research Council and Swedish Foundation of Strategic Research.

I may not remember someone that I met during the journey of my doctoral study even though I had a great help from them. I hope I can help others like who did to me. My heart will remind me of him or her sometimes.

I have been really joyful with all my friends and seniors during my PhD study period. I am happy because of being together with sharing ideas and heart. Thank you for all your good will around me, wholeheartedly. I hope you a good luck in your life and to continue to keep in touch.

S. J. from Uppsala

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