Doctoral Dissertation (Shinshu University)

Development of shape memory polyurethane actuator and its applications

形状記憶ポリウレタンアクチュエータの開発と応用に関する研究

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Abstract

Shape memory polymers (SMPs) are a class of smart materials that can control shape by memorizing temporary shapes and returning to their original shapes. Particularly, shape memory polyurethane (SMPU) has become the favorite material for many desirable functions due to its high flexibility, high recovery, ease of processing, and low density. Especially, they are better in terms of biomaterials because they have biocompatibility and biodegradability. However, SMPU is an insulator material and has limitations for only thermal stimulus. To overcome this issue and interact with an electric response, an idea of electroactive polymer (EAP) was applied to conduct a dielectric elastomer actuator, which is a class of EAP used in many interesting applications, including artificial muscles, sensors. For integrating with biomaterials, Young's modulus of human skin or implants is generally less than 100 MPa, which is much lower than pure SMPU film's stiffness. Incorporating plasticizers such as dibutyl adipate (DBA) is an excellent candidate to enhance SMPU softness and perform gel-like soft films. Moreover, it can increase the polar attraction between the polymer and plasticizer, which contributes to improving the dielectric properties of SMPU composites. This dissertation develops SMPU gels focused on biomedical applications and demonstrates a new self-healing feature of soft actuators, which could activate both the thermal and electric stimulus. The main results are obtained as follows

(1) The preparation of SMPU gels for soft actuators has two main factors to focus, which are softness and dielectric properties. The softness of SMPU gels was improved close to a human implant, which is the energy dissipation factor of approximately 0.2–0.5, and the dielectric constant at 1 Hz in SMPU gels was significantly improved from 2.9 to 153 by the addition 2 times of DBA plasticizer, which allows the developed SMPU gels to function as sensor and actuators under applied electric fields with frequency dependence. The impedance control can allow for velocity control in robotic applications to imitate human motion. This could predict the further response of electric actuation.

(2) The actuation of electric and thermal was studied. Electric actuation of dielectric SMPU gel actuator was conducted with conductive materials charging, and its two-way shape deformation of contraction and expansion was investigated over several electric on-off cycles. The largest contraction reached 6.76% with an electric field of 3.42 V/μm. The thermomechanical analysis showed that SMPU gels could be stretched up to a high strain of 80% and showed immediately shape recovery behavior for the SMPU gels. The developed

dielectric SMPU actuator displayed the ability to respond to thermal and electric stimuli. These composite materials have the potential for alternative actuation applications, including biomaterials.

(3) Thermal actuation has been focused and adjusting the transition temperature of SMPU gels to activate the human body temperature range and design its applications for tube actuation. The plasticized SMPU tube was activated at 37 °C, faster than the pure SMPU tube. The effect of thermal triggering on tensile and viscoelastic properties was investigated, and according to thermomechanical analysis results, the shape recovery ratio of tensile deformation is up to 99%. Adding DBA plasticizers to SMPU demonstrated a quicker recovery rate than pure SMPU during tube compression and expansion on diameter direction. In addition, according to thermomechanical analysis results, the shape recovery ratio of tensile deformation is up to 99%.

(4) One of the most popular processing shapes for producing smart biomaterial devices is the tube actuator, especially for biomedical applications such as stents and artificial blood vessels, which can function in round shrinking and expansion deformation via diameter direction. We have fabrication two kinds of tube actuators. The first is developed for heat actuation. The tube compression and expansion demonstrated tube recovery in the diameter direction up to 83% for SMPU/DBA gel, and their large recovery behavior started from 37 °C. Their tube recovery acts with 30 s via 40 ºC. Another is developed for electric actuation. CNC was incorporated into their composites to enhance the dielectric properties of SMPU and DBA composites to obtain the large deformation and fast response on electric actuation. The displacement on contraction and expansion was enhanced up to 11.58% on thickness direction. Furthermore, its tube contraction was occurred up to 800 μm (0.02% of its diameter direction).

(5) The biocompatibility in vitro experiment was conducted to address the possibility of biomedical applications. The cell adhesion showed that these gels have non-toxicity, and the cell proliferation demonstrated the cell growth on SMPU/DBA and SMPU/PEG. It indicated that they are not hindering cell growth. In addition, the cell adhesions and proliferation of NH3T3 mouse cells in vitro experiments supported their ability of biocompatibility.

As a total, we designed the developed SMPU, and the dielectric elastomer actuator displayed a multifunctional response to thermal and electric stimuli. For mechanical properties, the fast response, high recovery, and small stress were excellent features to be safe for use in the human body. These SMPU gel and its tube actuators can be used in the human body, which

has aided our work on drug release systems for biomedical applications. In the future, SMPU gels are also expected to be used in producing thermal and electric tube actuators for microactuators, drug delivery, artificial blood vessels, and other aspects of tissue engineering.

Content

Chapter 1

General introduction

Chapter 1 General introduction

As the average human age in global society increases, biomaterials can play important roles in medicine to support weak organs and help to extend lives. The effects of some injuries and diseases can be addressed using artificial equipment to allow the complete function of the human body. To combine natural compliance with controllable actuation, soft polymer materials were developed because they are softer and more comfortable inside the human body than traditional materials. With the progress of technology in biology and engineering, new synthetic materials with improved properties have been developed. Smart materials are attractive candidates as biomaterials. In particular, the properties of smart materials can be adapted to display potential functions and can be modulated through appropriate control by external stimuli such as stress, temperature, moisture, electricity, magnetic fields, light, and chemical components. Smart materials are the basis of devices used in a wide range of applications, including sensors, actuators, artificial muscles, and electroactive polymers. An appealing prospect is to integrate biomaterials and smart materials together to develop new products to solve issues associated with human aging.

1.1 Smart materials

Smart materials are intelligent or responsive materials that can be controlled by appropriate stimuli, such as heat, light, stress, and electricity. The properties of these innovative materials can be designed for specific applications. Smart materials could be developed for use in various applications, including sensors, actuators, and as biomaterials

The development of smart materials involves multiple research fields from all over the world, including physics, chemistry, computer science, applied science, and engineering. The study of composite materials and their structure contributes to the wide applications of smart materials. Smart materials have been successfully used in applications and research on the development of optimized smart materials is increasing. [1-2]

Smart materials and technology have been combined to realize various applications, especially in communication technology. It is anticipated that humans will make wide use of smart materials in the future. In daily life, there are now several examples of smart materials used in home and textile applications. Smart materials can act as actuators or sensors; that is, their properties are changed by suitable environmental conditions. This feature makes smart

materials attractive for use in healthcare products and monitoring systems. The development of new smart materials and advanced technologies could facilitate human activities. [3]

1.2 Shape memory polymers

Shape memory polymers (SMPs) are a class of smart materials that have the ability to return to their original shape after temporary deformation induced by an external stimulus, such as temperature or electricity. SMPs possess multiple advantageous properties including light weight, high recoverability, transparency, chemical stability, modification potential, easy processing, biocompatibility, and biodegradability. [4] The unique property of SMPs is their ability to deform and then recover to their original shape. SMPs contain two phases: a fixed phase and a reversible phase.

The shape memory process has three steps. Firstly, the sample is deformed from its original shape to a temporary shape. This step takes advantage of the thermal transition temperature of the sample. That is, the material can be deformed at high temperature and then fixed at low temperature. The second step is storage of the material in its deformed shape. The third step is the recovery of the material back to its original shape when the temperature is raised above its thermal transition temperature. [5] The hard and soft segments of an SMP can be controlled by its components, allowing polymers that show good shape fixity and recovery to be developed. [6,7]

Shape memory properties can be described by the shape memory recovery ratio (Rr) and shape memory fixity ratio (Rf). [7] Rr and Rf can be calculated using the formula below:

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)} \text{ x } 100\%, \qquad (1\text{-}1)$$

$$R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m} \text{ x } 100\%, \qquad (1\text{-}2)$$

where ε_m is the strain at constrain rate, ε_u is the strain at recovery, ε_p is the residual strain after recovery, and N is the number of cycles.

The properties of SMPs and shape memory alloys (SMAs) are compared. They reveal that SMAs are better in terms of recovery stress, whereas SMPs have higher recovery strain than SMAs. Both of these materials can be adjusted between hard and soft by changing the temperature. The density, cost, and thermal conductivity of SMPs and SMAs are different benefic in applications. The shape memory effect contributes to the development of new shape memory materials suitable for desired applications. [8]

In 1932, Chang and Read discovered the shape memory effect, which was the first step in the field of active materials research. [9] In 1940, Vernon et al. [10] described their discovery of shape memory in a US patent on dental materials (methacrylic ester resin). In the 1960s, an SMP based on polyethylene displaying heat shrinkability was developed. [11-12] In 1963, the discovery of the shape memory effect in equiatomic nickel–titanium alloy greatly increased interest in SMAs for commercial applications because of their combination of a desirable transition temperature close to body temperature, high elasticity, biocompatibility, and a two-way shape-memory effect. This alloy has a shape memory effect because it can be deformed, fixed into a temporary shape, and then recover back to its original shape. [13-14] In 1980, shape memory polyurethanes (SMPUs) were first developed in Japan. Over many years, new materials based on PU with shape memory were developed and used in a wide range of industrial applications. [20] In 1984, the SMP with the trade name Polynorbornene was first developed by CDF Chimie Company in France. [15]

1.3 Synthesis of shape memory polyurethane and its composites

A shape memory polymer based on polyurethane is a polymer with long tangled linear polymer chains that display a shape memory effect. PU is a good candidate for shape memory materials because it is composed of soft and hard segments as shown in Fig. 1-1. The hard segments of SMPUs contain diisocyanate groups such as 4,4-diphenylmethane diisocyanate (MDI), phenylene diisocyanate (PDI), toluene diisocyanate, hexamethylene diisocyanate, or isophorone diisocyanate (IPDI). Soft segments of SMPUs are usually polyols, which show good flexibility and low transition temperatures because they possess an aliphatic structure and readily form intermolecular interactions because of their abundant ether bonds. [16] Increasing the content of hard segments of SMPUs can enhance their mechanical properties because they contain more dipole-dipole and hydrogen bonding interactions, which leads to a higher degree of crystallinity. [17] Compared with regular PUs, SMPUs consist of longer soft and hard

segments and also contain rigid chain extenders, which allows higher deformation and larger recovery stress. The copolymerization of urethane chains as soft segments increases flexibility, which is desirable to realize shape memory behavior. [18]

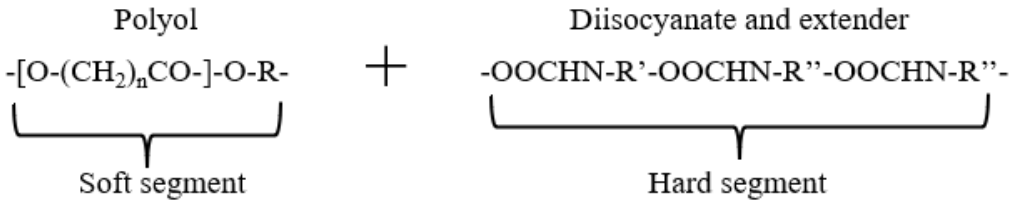

Fig. 1-1 Structure of SMPU

SMPUs are becoming popular in various applications. However, SMPUs suffer from drawbacks including low Young's modulus, strength, stiffness, and thermal conductivity as well as slow response to an electric field. Therefore, the properties of SMPUs need to be modified. To break though these limitations of the properties of SMPUs, shape memory composites (SMCs) have been developed. SMCs are fabricated by incorporation of organic or inorganic fillers into SMPs, which can enhance mechanical, electrical, and thermal properties. Therefore, SMCs respond to stimuli and behave as actuator materials more readily than SMPUs.

1.4 Dielectric elastomer actuator

Several soft actuators have been developed for a wide range of applications. Soft actuators have been produced using polymers and gels, including synthetic polymers such as silicone rubbers and polyurethane (PU). Furthermore, some natural polymers, such as DNA and proteins, can also be used to develop soft actuators. Soft actuators can be produced using various types of gels such as hydrogels, oil-based gels, and aerogels. Another unique feather of gel actuators that it is easy to control their mechanical properties and programming using external stimuli. A plasticizer is a polymer additive that is used to enhance polymer properties. Plasticizers are generally added to polymer films and coatings to increase flexibility. They have the ability to control the glass transition temperature of polymers and decrease their rigidity. Plasticizers are typically dipolar molecules such as poly(vinyl chloride) and cellulose. In polymers containing plasticizers, there are intermolecular forces between the plasticizer molecules themselves and between the plasticizer and polymer molecules. The negative and positive dipoles of the dipolar molecules interact with each other. Additionally, hydrogen

bonds involving groups such as C=O, O-H and N-H are present in some polymer structures. Hydrogen bonds help to form strong interactions between plasticizers and polymers. Some of the properties required for plasticizers are low volatility, high-temperature stability, light stability, and no odor. [19] Dialkyl adipates are common plasticizers used in a wide range of applications. Dialkyl adipates are liquids consisting of small diester molecules. Dialkyl adipates are attractive plasticizers because they possess several advantages such as low vapor pressure, low freezing temperature, high boiling temperature, relatively low viscosities, high chemical stability, and environmental friendliness. [20-21]. Gel actuators have the ability to be lightweight, biocompatible, biodegradable, and easily processed [22]. A study reported that the change in the osmotic pressure inside a polymer gel causes it to swell or shrink [23]. The displacement of the self-oscillating gel is on the micrometer scale. The small displacement of the gel might be overcome by the incorporation of materials with greater displacement.

1.5 Various Applications

SMP are important because of their potential in a large range of applications in human daily life around the world. SMPs could be developed for biomedical applications [24-25]. Because of their various unique features, they are considered attractive for aerospace applications. Additionally, SMPUs have been used to construct actuators and sensors [26] and been employed in other applications [27].

Biomedical applications

In the past, metal and shape memory alloys were commonly used in the domain of biomaterials. However, there are several drawbacks associated with the use of metallic stents. Since its stiffness caused pain to the human implant and mismatch with the arterial wall. Moreover, the fabrication process is difficult, and the cost is high [28]. To replace shape memory alloys, SMP especially for SMPU, became highly interesting to develop their potential as biomedical applications to replace the SMAs. SMPU has been considered for biomedical applications because of its two interesting, unique features that are particularly suited for the medical field. First, SMPUs are non-toxic and biocompatible, making them suitable for usage inside the human body. Second, the shape of SMP has excellent performance for temperature control [29], and their transition temperatures could be controlled in the range of human body temperature. The advantages of the shape memory effect to perform the shapes and return to their original shapes endow the potential function for self-healing or deploying some injure for

any human surgeries. SMPU has been developed and applied to use as wound closure [30], and the suture could be adjusted loosely in its temporary shape under applied stress. When the temperature is increased above the transition temperature, the suture will shrink and then tighten the knot. Since there is maximum recovery stress occurring, which is very small and safe for human body implants. Moreover, some researchers [31] have been studied the SMP effect for a vascular stent with a drug delivery system.

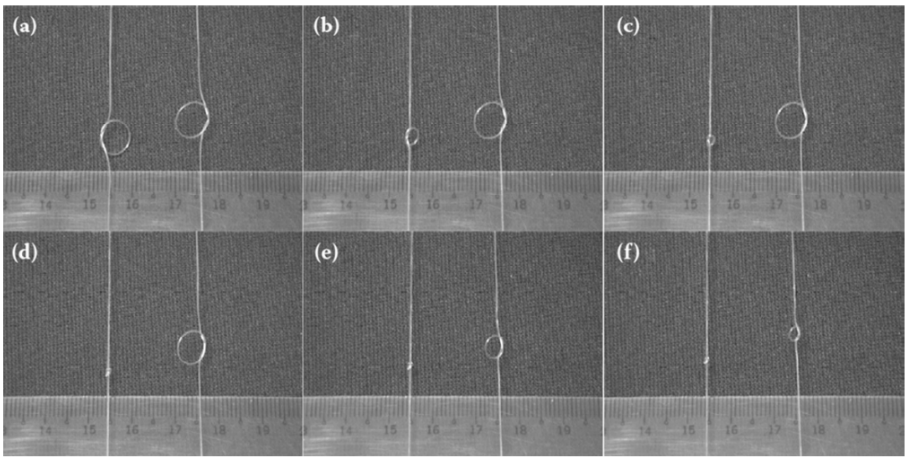

Fig.1-2 temperature-induced shape memory knot [30]

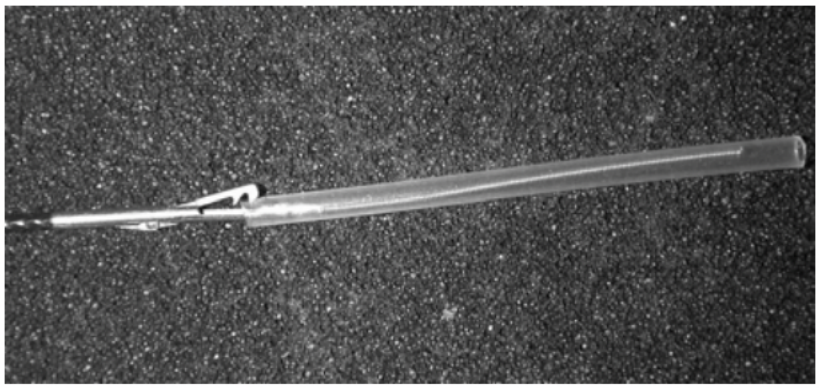

Fig. 1-3 Shape memory recovery for drug delivery system [31]

Aerospace applications

Shape memory composites (SMCs) are attracting interest for use in aerospace applications because of their lightweight, easy shape control via temperature, and shape transformation ability [32], compared to shape memory alloys. It is necessary to integrate mechanical and other functional properties to create new materials based on SMCs to meet aerospace requirements. Therefore, SMPCs in space-deployable structures can support flight vehicles such as speed and low energy consumption. SMCs with a sandwich structure has been fabricated. For example, a thermosetting carbon-fiber-reinforced material was used for the outer part of the SMC, and a thermosetting epoxy resin was used as the shape memory interlayer [33], and it was heated in an oven and showed good shape recovery.

Moreover, Lockheed Martin's concept [34] had proposed Z-shape morphing aircraft. The shape memory polymer was used to control the expansion wings when the heat was applied. Santo et al. [35] had studied the SMC for self-deployable structures, and the SMC cross and SMC frame consisted of a thin aluminum sheet. Their structure exhibits the possibility of deploying configuration.

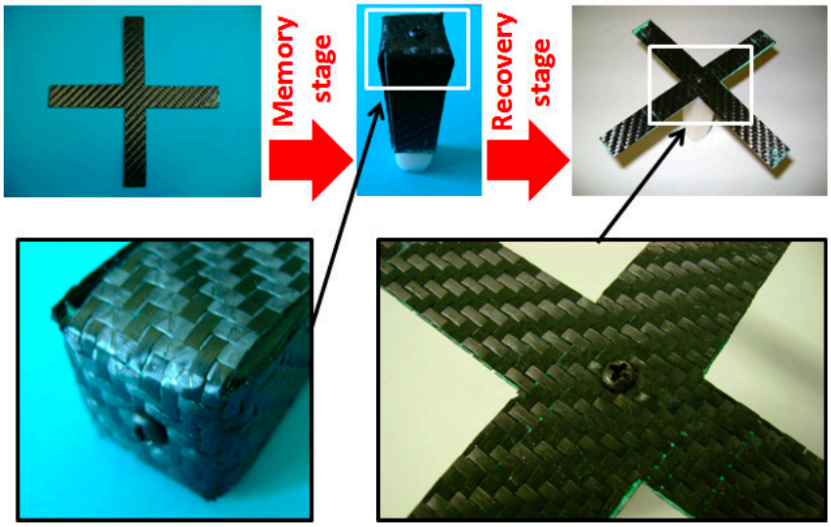

Fig. 1-4 SMC cross structure [35]

Other applications

Shape memory materials can be used as textiles for clothing and other applications [36]. For example, Dermizax developed a shape memory polymer for microclimates [37]. The membrane between the polymer molecules is expanded when the fabric moisture increases. Sphere React Shirt [38] has been fabricated to be activated with human body temperature. This shirt has vents on it when the user starts to make performance because of the high temperature of the body. If the user's temperature is high, the vents of shirt become open, and the air can go through for sweat. Furthermore, there are plenty of lists for SMP applications, which could be used to develop packaging, underwear, home appliances, and automatic electronics [39].

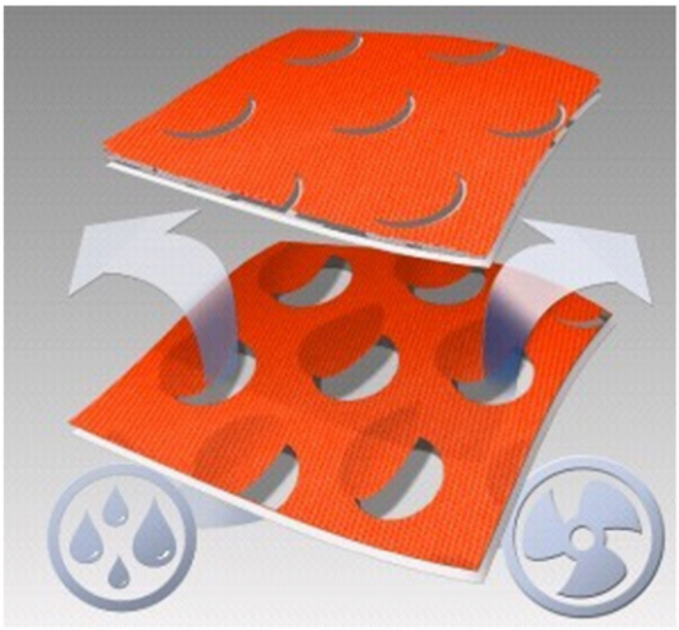

Fig. 1-5 Sphere React Shirt [37]

1.6 Purposes and significances of the research

This research aims to develop a new multifunctional soft actuator integrating shape memory effect to apply with injuries or diseases and support a negative impact on human life and the average human age in a global society. It is necessary to discover new materials that play an important role in biomedical applications. SMPU gel actuators are an excellent candidate for the next generation of biosensors and actuators and demonstrate the unique properties of shape memory property.

In this PhD thesis, we proposed to develop a novel soft actuator-based shape memory polyurethane as SMPU gels with having both electric and thermal responsive performance They will present the two-way contraction and expansion movement under the low frequency of impedance and their low recovery stress occurring on thermal actuation will represent to their safety to use inside the human body. Moreover, the shape memory fixity and recovery of SMPU gels under the number of cycles will be observed to exhibit their cycle life. Since their structures have hard segments and soft segments, which are easy to control by adjusting the segments, their glass transition temperature was also constructed in the range of human body temperature activation.

Finally, we developed SMPU gels for tube actuators, which are easy to use in the biomedical field, and applied the thermal and electric actuation on the diameter direction. Using these SMPU gels as tube actuators will be demonstrated. The biocompatibility of the prepared SMPU gels and their composites will be also confirmed by an experiment of mouse cell culture. They could be the realization of smart-biomaterials for biosensors, artificial muscle, and artificial blood vessels.

1.7 Outline of this dissertation

This study developed a shape memory polyurethane (SMPU) gel actuator with DBA plasticizers because of the increased environmental friendliness of polyurethane, and it confirmed the possibility of replacing other materials, which might be not safe for human body use. The use of DBA plasticizer and other filler such as PEG and CNC on SMPU matrix is expected to enhance the dielectric property of SMPU and decrease the interaction between polymer matrix, resulting in softening SMPU being gels. Moreover, SMPU gel actuators also demonstrate thermal activation ability. This is challenging work to develop multifunctional stimuli-responsive materials. Besides, all components are friendly to the human body and environment. which is expected for use in the bioengineering field. This research mainly includes the following aspects by the chapters below:

In the chapter 1, the general introduction has been explained about the background, state of art for developed shape memory polymer and its composites, and purpose of this dissertation.

In the chapter 2, the fabrication of an SMPU gel incorporating plasticizers by the simple solution casting method. In the biology field, most soft tissues can be considered gels if we define gel-like soft films as soft polymeric composite material. (1) The young's modulus was significantly decreased with the increasing amount of DBA up to 15 times (SMP-4DBA) compared to SMP neat. Storage modulus also became decreased and switch the glass transition temperature range from SMP. It indicated that DBA is successful in improving the softness of SMP materials and is easy to deform at a lower temperature. (2) The dielectric constant was also investigated to explain their dielectric properties. These are two main factors to develop SMPU gels for electric actuation.

In the chapter 3, The SMPU gels were actuated by thermal and electric actuation. Moreover, its electromechanical performance and mechanism were explained. The shape recoverability was studied by thermally induced. SMP incorporating with DBA is much higher strain compare with SMP neat. The shape memory effect of SMP-1DBA and SMP-2DBA could be rapidly recovered after removing stress, much faster than was the case for neat SMP. The shape recovery ratio is more than 90% and trend to increase with the number of cycles. DBA could change SMP property from insulator to dielectric. The dielectric constant of gel was improved and SMP-2DBA has greatest dielectric constant value.

In the chapter 4, The SMPU gel for thermal actuation was improved by adjusting the concentration of plasticizers and designing methods for tube actuators. Their softness and glass transition temperature were switched close to human body temperature. The plasticized SMPU tube was activated at 37 °C, which is faster than the pure SMPU tube. The effect of thermal triggering on tensile and viscoelastic properties was investigated. SMP tubes were fabricated and demonstrated in shape memory test of round shrinking and expanding direction by specific compression programmed method.

In the chapter 5, The SMPU gel tube for electric actuation was developed by adding CNC to SMPU gel composites to obtain better performance on dielectric properties. Moreover, their glass transition temperature was enhanced close human body temperature range. The tube deformation on electric actuation occurred in the diameter direction on contraction and expansion, which is deformed in a micro-scale actuator.

In the chapter 6, these SMPU gel actuators are expected to use for biomedical applications. The biocompatibility in vitro experiment was conducted to investigate their non-toxicity. Therefore, cell cultures of four kinds of SMP samples (SMP, SMP-DBA, SMP-PEG) were used to investigate cell adhesion, proliferation, and morphology. All samples do not have toxicity. From SEM photograph, the shape, and variation of cell exhibit of the living sign. Additionally, SMP and SMP-DBA cell proliferation has better biocompatibility than SMP-PEG due to the number of living cells. Finally, the general conclusion of this dissertation was explained in the chapter 7.

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Chapter 2

Preparation of SMPU gels

Chapter 2 Preparation of SMPU gels

2.1. Introduction

The shape memory effect was first discovered by Chang and Read in 1932 and it gave rise to research in the field of active materials [1]. Over the subsequent years, shape memory polymers (SMPs) were developed and have been used in a wide range of industrial applications [2]. Because of their unique features, SMPs have been applied in various applications, including as biomedical materials [3,4], aerospace structures [5], actuators, and sensors [6,7]. SMPs are a class of smart materials that have the unique ability to return to their original shape after temporary deformation induced by an external stimulus, including temperature, magnetic field, or electric field. SMPs possess multiple advantageous properties including low weight, flexibility, and easy processing [8]. They usually have good shape memory behavior when controlled by direct heating [9,10], and display fast actuation on exposure to a simple external thermal gas or liquid. Many reports have investigated the SMP effects of polyurethane and poly(e-caprolactone) [11–14], the composites of two or more different phases were studied to improve the shape memory effect. For example, polyethylene glycol enhances the soft segment of polyurethane [15-16] and the copolymer of rubber and PCL have good shape memory effect [17]. Moreover, the fast shape memory effect of controllable shape recovery in poly(ethylene terephthalate) on heating was reported [18]. Lendlein et al. described the mechanism behind the heating effects of shape-memory polymers [19] and Wu et al. reported the thermally induced phase switch of poly(e-caprolactone) for artificial muscle applications [20].

In this chapter, SMPU was combined with the plasticizer dibutyl adipate (DBA), then investigated on basic mechanical properties. The addition of DBA plasticizer resulted in the formation of a gel-like soft-film material. The softness and dielectric properties will be investigated to obtain the main key points to perform dielectric soft actuators.

2.2. Experiments

2.2.1 Preparation of SMPU/DBA gel

Thermoplastic SMPU pellets with a glass transition temperature (T_g) of 65 °C were obtained from Diaplex SMP Technologies Inc. (Mitsubishi Heavy Industries Ltd.), Japan. The plasticizer (DBA) and solvent N, N-dimethylformamide (DMF) were purchased from Wako Pure Chemical Industries Ltd. (Japan) and Sigma-Aldrich (USA), respectively.

A casting solution method was used to prepare the SMP gels. For this, 5 w/v% of the SMP pellets were dissolved in DMF for 24 h. Different contents of DBA were added to the solutions of SMP in DMF. The weight ratio of the SMP to DBA was adjusted from 1:0 to 1:4 and labelled as SMP, SMP-1DBA, SMP-2DBA, SMP-3DBA, and SMP-4DBA. The solutions were stirred for 3 days. Each solution was then cast into a petri dish and evaporated by heating at 65 °C for 5 days. The pure SMP film was transparent, and the soft gel-like films became translucent with increasing DBA as shown in Fig.2-1.

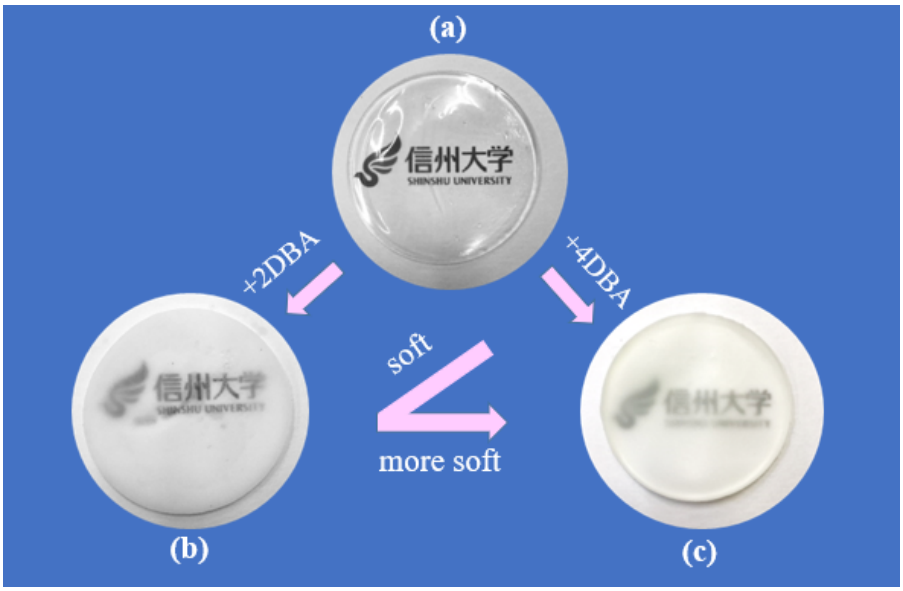

Fig.2-1 a), b), and c) Images of the samples SMP, SMP-2DBA, and SMP-4DBA, respectively

2.2.2 Tensile properties

The tensile properties of the SMP gels were investigated at 25 °C and 60% RH using a universal testing machine, A&D Co., Ltd., Tokyo, Japan. The load capacity and tensile speed were 50 N and 10 mm/min, respectively. Each type of sample was tested 3 times and the average value was used.

2.2.3 Impedance analysis

The samples were cut into circles with a diameter of 14 mm. The interaction between the polymer and plasticizer behavior was investigated using an impedance analyzer, Solartron 1260/1296, Toyo Technical Ltd., Japan. The experiments were carried out in the frequency range of 10^0–10^6 Hz at 100 mV. Each type of sample was tested 3 times and the average value was used. The dielectric constant (ε) and charge storage capacity increased but the interfacial

resistance decreased with increasing DBA content in the samples. This can be calculated by equation (6):

$$C=\varepsilon \cdot A/d, \qquad (2\text{-}1)$$

where C is the capacitance, A is the conductive area, and d is the distance between the conductors.

2.3. Results and discussion

2.3.1 Tensile properties

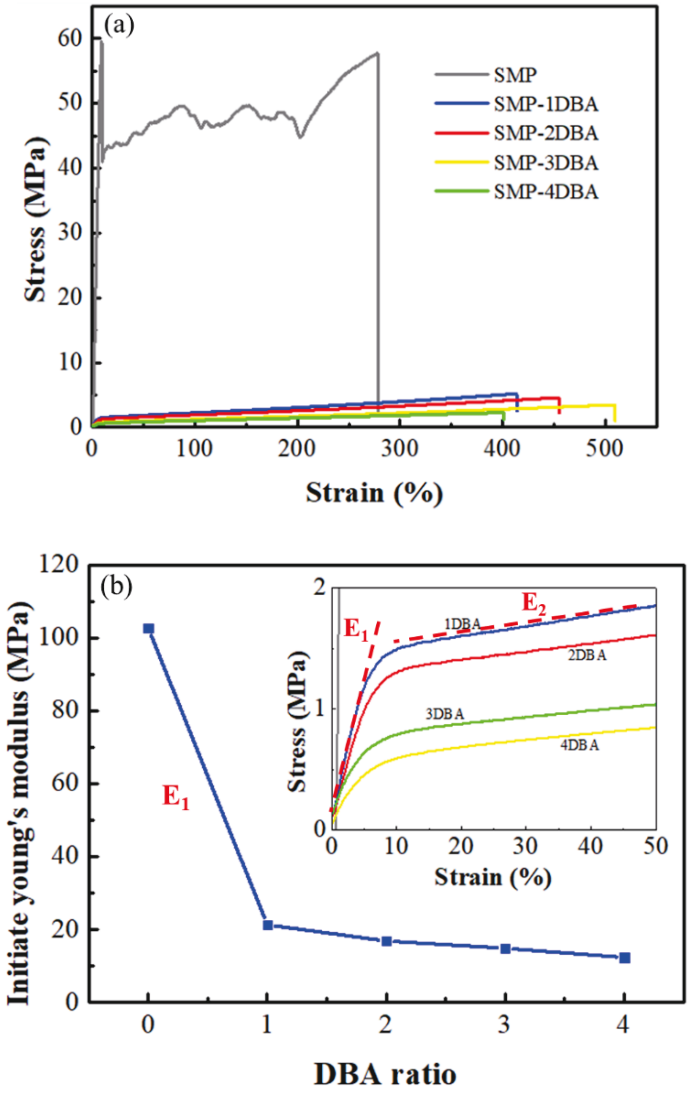

Fig.2-2 a) and b) Stress-strain curves and Young's modulus of the SMP and SMP gels with different DBA contents

Table 2-1 Young's modulus and strain of the neat SMP and SMP gels with different DBA contents

Sample	Young's modulus (MPa) (E_1)	Young's Modulus (MPa) (E_2)	Tensile strength (MPa)	Strain (%)
SMP	102.83	5.93	57.79	279
SMP-1DBA	21.35	0.79	5.15	413
SMP-2DBA	16.93	0.64	4.59	454
SMP-3DBA	14.93	0.44	3.44	509
SMP-4DBA	12.41	0.39	2.23	400

The tensile properties of the pure SMP and the SMP gels are shown in Fig. 2. The pure SMP sample has a large tensile strength at break of 57.59 MPa. The SMP gels displayed a significantly lower tensile strength, as outlined in Table 2, with an observed 11.22 times decrease for SMP-1DBA compared with SMP. The initial Young's modulus (E_1) shows the relationship between the stress and strain (Fig.2-2b), which is key factor for use as a DE actuator. The E_1 of the pristine SMP at a small strain was 102.83 MPa, which indicated a higher stiffness. Incorporation of the DBA plasticizer resulted in increased SMP softness, which led to a smaller Young's modulus. This resulted in a decrease of up to 8.29 times for SMP-4DBA compared with pure SMP. Furthermore, the strain at break for all the SMP gels increased to 400–500%, which was an improvement over the pristine SMP at 279%. Furthermore, the Young's modulus (E_2) was also measured at a large stretching strain to determine the strain hardening. In this region, there was a large increase in the strain rate with only a small increase of stress. The values significantly decreased about 7.5 times for the lowest DBA content (SMP-1DBA), and then gradually decreased with increasing DBA content. The samples displayed plastic deformation as well as increased elongation time and total large stretching before breaking. Therefore, increased elongation occurred with less applied force. This indicated that the elastic and plastic deformation properties of the material improved. The increased flexibility of the plasticized polymer resulted in a smaller Young's modulus, smaller strain hardening modulus, a lower tensile stress, and larger strain. This indicated that the plasticizer diffused into the polymer matrix and created a looser structure because of secondary bonding forces. For practical application of these SMP gels, the material needs to be soft and easily deformable.

2.3.2 Dielectric properties

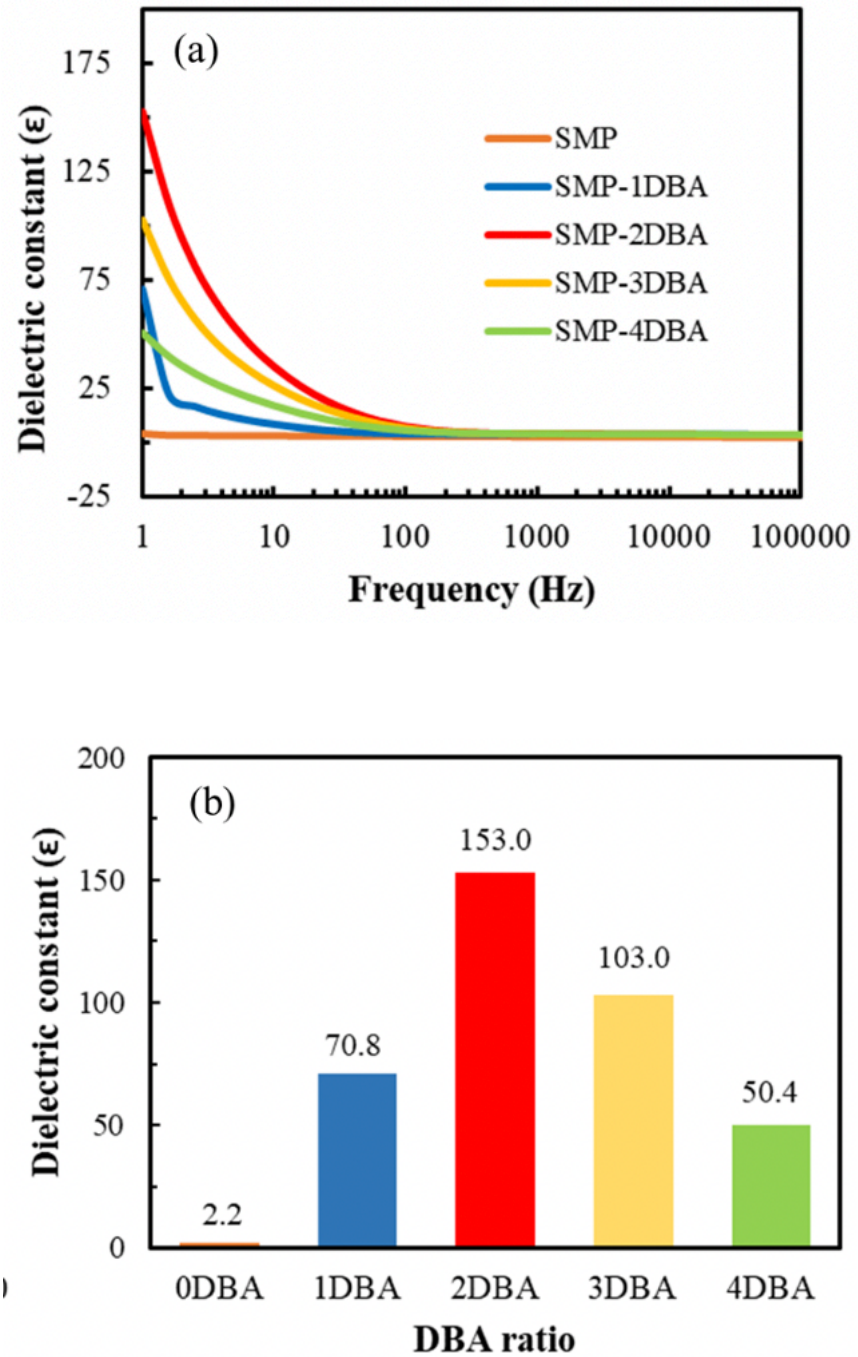

Fig. 2-3 a) Dielectric constant of the SMP and SMP with different DBA contents and b) at 1 Hz

The dielectric elastomer requires an external electric field to activate the material. Hence, the dielectric properties of the SMP gels are very important for development and use of DE actuators based on the principle of Maxwell stress, as demonstrated in equation (2-1), where the dielectric constant is a major parameter. Additionally, for the electrostriction phenomenon, strain is also caused by a change of the dielectric constant.

Figure 3a shows the results of the impedance analysis of the pure SMP and the SMP gels with different DBA contents. The dielectric constant of the pure SMP has a very low value of 2.2, and it was constant for all the investigated samples because of their insulator property. However, on addition 1 time of DBA, the dielectric constant at low frequencies sharply increased to 70.8, which was about 32 times increase compared with the pure SMP. Figure 2-3b shows the results of the impedance analysis of the frequency at 1 Hz. We found that the SMP-2DBA sample had the largest dielectric constant at 153. The dielectric constant of SMP-3DBA was lower than SMP-2DBA, but it was still good sufficient to drive actuation on the intensity of electric field. These results would affect to the electric actuation. The largest dielectric constant expressed in largest contraction on the intensity of electric field. The SMP-4DBA sample had the lowest dielectric constant, and it was quite difficult to activate actuation via the electric field and smallest contraction on electric actuation. This behavior can be attributed to the limited interaction between the polymer and plasticizer because of the rich phase of plasticizer. Therefore, the dielectric properties of the SMP gels were closely related to the plasticizer properties. Furthermore, for the samples with DBA, the dielectric constant gradually dropped to a constant value as the frequency increased to 10 Hz and became constant above 1000 Hz. The dielectric constant of the SMP gels had a significant frequency dependence in the low-frequency regime. Therefore, the observed dielectric properties would support the electric actuation of the SMP gels observed in the next experiments. Moreover, impedance control can allow for velocity control in robotic applications for imitation of human motion, this could also be further aided by the softness and dielectric properties of the material.

2.6 Conclusion

In this work, SMPU/DBA gel-like soft films were fabricated and their characterization on tensile and dielectric properties was observed to measure the two main factors on electromechanical performance. From their young's modulus and dielectric constant, SMPU/2DBA have the best potential to perform the electric actuation. The addition of DBA enhanced the softness of gels and markedly increased the dielectric constant. The dielectric constant in SMPU gels was clearly improved at 1 Hz, which allows the developed SMPU gels to function as sensors and actuators under applied electric fields with frequency dependence.

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Chapter 3

Actuation and mechanism of SMPU gel actuators

Chapter 3 Actuation and mechanism of SMPU gel actuators

3.1. Introduction

Shape memory polyurethane (SMPU) dielectric elastomer (DE) actuators have certain unique attributes beyond their ability to be deformed and recover their initial shape, including the ability for control via direct heating. SMPU structures are composed of two parts: hard segments [1] with a high degree of crystallinity that functions as a fixed phase; and soft segments that are usually polyols with good flexibility and low transition temperatures (T_{trans}). The polyols in the soft segments have an aliphatic structure with a significant number of intermolecular interactions because of their abundant ether bonds [2,3]. When $T>T_{trans}$, the material has high elasticity and flexibility that is expressed as a recovery effect. When $T<T_{trans}$, the polymer chains are temporarily fixed in their current shape. The hard and soft segments of the SMPU can be controlled via their constituent compounds, resulting in good shape fixity and recovery. Furthermore, SMPUs have shown good biocompatibility and environmental degradability, which is favorable to develop of biomedical devices for practical uses.

For electric-stimulation-based actuators, a high dielectric constant (ε) of the active material is a key factor. However, most SMPs are insulating materials and have a slow response to electric stimulus. Hence, conductive fillers are required for improved conductivity. For instance, carbon-based SMP composites exhibited electric-actuation control [4,5]. Carbon nanotube treated PU improved recovery speed and U shape composite fast recovered their shape by electric voltage. Furthermore, Li et al. fabricated hand-shape actuator by addition CNTs to buckypaper [6]. These fillers are very popular to conduct the conductive materials, but they have some drawbacks for using with human body and environment.

To overcome the heat stimuli limitations of SMPs, an electroactive polymer (EAP) was used to form a dielectric elastomer by using plasticizers in a polymer may also increase the polar attraction between the polymer and plasticizer, which results in an increased dielectric constant (ε), which are a class of EAP has been used in many interesting applications, including as artificial muscles, sensors, and actuators [7-9]. Perrone et al. carried out experiments on a silicone actuator [10] and many researchers have reported PVC-based actuators for practical application [11-14]. Because of their expected quick electric response rate, large deformation, and control at room temperature, plasticized gel actuators have become increasingly attractive for applications such as micro lenses, hydraulic or pneumatic systems, and as biomaterials [15]. Based on the DE actuator concept, two key electromechanical factors are required for

realization of a large actuation strain by an electric field: the first is a small Young's modulus (Y), resulting in easy deformation; the other is a high dielectric constant (ε) to achieve a good response to the applied electric field. The deformation of a DE actuator follows the Maxwell stress principle [16]:

$$S_z = -\varepsilon_0 \varepsilon (V/Z)^2/Y \qquad (3\text{-}1)$$

where S_z is the strain, ε_0 is the vacuum dielectric constant, V is the electric field, Z is the thickness, and Y is Young's modulus. When an electric field is applied between the polymer and the electrodes, deformation occurs in the thickness direction. The use of a plasticizer can increase the softness of the polymers, i.e., a small Young's modulus, to realize the desired properties. Polymer plasticizer addition can create jelly-like soft materials because they diffuse into the polymer molecule and increase the free volume. This interaction results in softer materials. Additionally, many studies [17] have compared the use of DBA with other plasticizers such as dioctyl adipate (DOA). The DBA structures consisted of smaller diester molecules, and it was found that its molecular weight was more desirable for soft actuator applications. Especially, DBA have tested of non-toxicity for human body implant [18]. Researches in our laboratory also studied polyurethane actuator with DBA plasticizers because of the increased environmental friendliness of polyurethane, and it confirmed the possibility of replacing PVC, which might be not safe to human body use [19-22]. Therefore, shape memory polymer (SMPU) softened by DBA is another preferable to innovate soft actuator, no one conducted DBA with SMPU before. The use of DBA plasticizer on SMPU matrix is expected to enhance dielectric property of SMPU and decrease the interaction between polymer matrix, resulting in softening SMPU being gels. Moreover, SMPU have thermal activation ability, which is difficult for TPU. This is challenging work to develop multifunctional stimuli-responsive materials. Besides, all components are friendly to human body and environment. which is expected for use in bioengineering field.

To study the electromechanical actuation, in this chapter SMPU actuators were fabricated using an active SMPU sandwiched between a metal mesh and a foil that served as the electrodes. The electric actuation performance was investigated in the thickness direction for two-way shape deformation of contraction and expansion on applying of varying electric fields. The dielectric properties were optimized to support deformation of the SMPU gels and to realize a large actuation behavior. The chemical structures were investigated to confirm the material properties and clarify the actuation mechanism on electric stimulation. The results of

this work provide a foundation for further work on SMPU soft materials and their potential application for microactuators, artificial muscle, and biomaterials.

3.2. Experimental

3.2.1 SMPU observation by heating

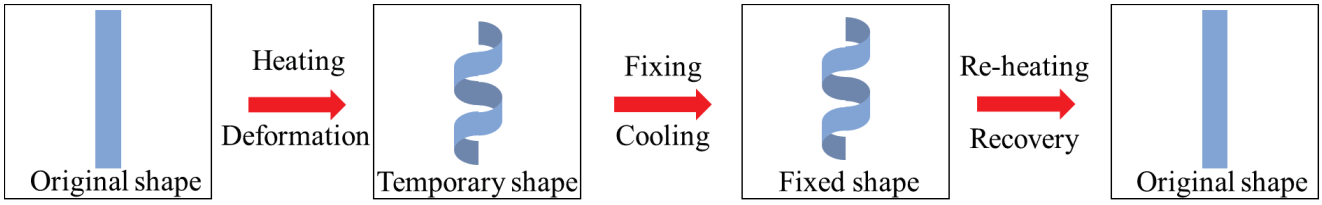

Fig.3-1 Shape memory process by heating

The samples (SMP and SMP-1DBA) were cut into rectangles with dimensions of 40 x 10 mm. A glass tube was used to create the temporary spiral shape at 80 °C, and it was fixed in cold water with an ice pack at 5 °C for 5 mins. The fixed shape was then placed in hot water and video of the shape recovery behavior was recorded. The SMP and SMP-1DBA samples were then compared.

3.2.2 Thermomechanical analysis

The shape memory effect was measured via thermomechanical analysis using the tensile testing method at different temperatures and applied stresses. This analysis was performed in five steps, as shown in Table 3-1.

Table 3-1 Thermomechanical program used for the experiments

Step	Temperature (°C)	Holding (min)	Stress (MPa)
1	30 → 65	20	0.01
2	65	15	0.6
3	65 → 30	4	0.6
4	30	5	0.01
5	30 → 65	20	0.01

The shape recovery and shape fixity ratio were calculated using equations (2) and (3) below:

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)} \times 100\%, \quad (3\text{-}2)$$

$$R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m} \times 100\%, \quad (3\text{-}3)$$

where R_r is the shape recovery ratio, R_f is the shape fixity ratio in each cycle, ε_m is the maximum strain at high temperature, ε_p is the residual strain at low temperature, ε_u is the strain at low stress after cooling, and N is the number of cycles.

3.2.3 Electric response

The gel samples were cut into rectangles with dimension 20 x 20 mm. The gel actuator was prepared by sandwiching the active SMP between the metal electrodes (Fig. 3-2a). An electrical charge was applied from the foil cathode into the gel; the electrons migrated through the SMP gel toward the stainless mesh anode. The surface properties of the gel allowed for facile stacking with the electrodes. The displacement was observed in the thickness direction using a laser displacement meter LK-G3000, Keyence Co., Japan (Fig. 3-2b). The test was performed at 0.07 Hz and recorded for 28 s. The SMP-2DBA gel was tested in the range of 100–800 mV to study the actuation performance.

To accurately compare the actuation of the samples under different electric fields, the gel thickness between the samples was measured and controlled to realize field intensities of 3.24 to 34.24 V/um. The electric field (E) can be calculated via equation (3-4):

$$E = V/d, \quad (3\text{-}4)$$

where V is the applied voltage and d is the thickness. The DC field was cycled on-off 6 times. The maximum deformation for each cycle was taken as an average and the %contraction strain of SMP gel was obtained by:

$$\%\text{Contraction strain } (\varepsilon_d) = \frac{|d|}{D_o} \times 100, \quad (3\text{-}5)$$

where d is the contraction and D_o is the original thickness.

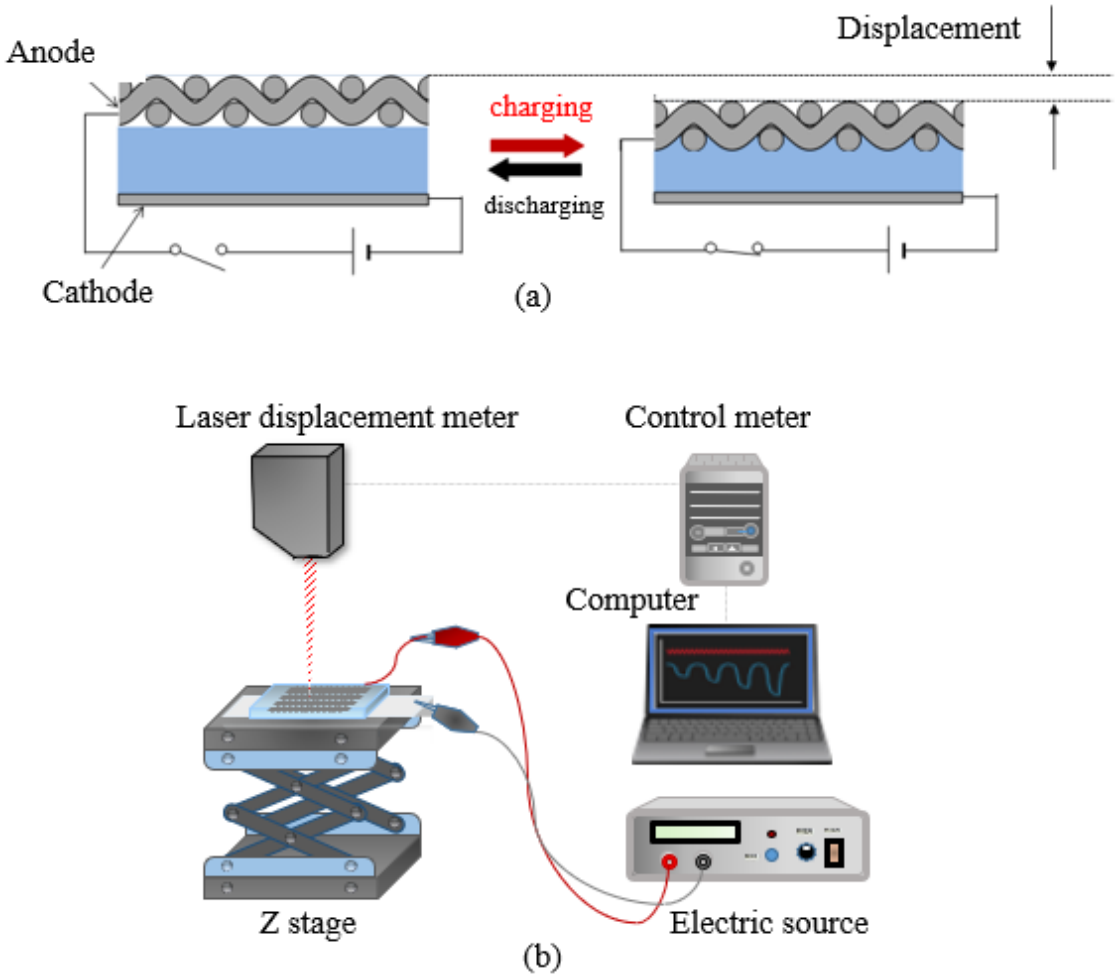

Fig.3-2 a) Schematic of deformation of the SMP gel actuator on DC discharging and charging and b) setup for the deformation experiments by electric actuation

3.2.4 Fourier-transform infrared spectroscopy (FTIR)

The chemical structures of the pristine SMP and SMP gels were investigated via FTIR, Shimadzu IR Prestige-21, Japan. The FTIR spectra of the thin films were analyzed in the range 500–4000 cm^{-1} at room temperature.

3.3 Results and discussion

3.3.1 Shape memory property characterization

3.3.1.1 Thermal SMPU behavior

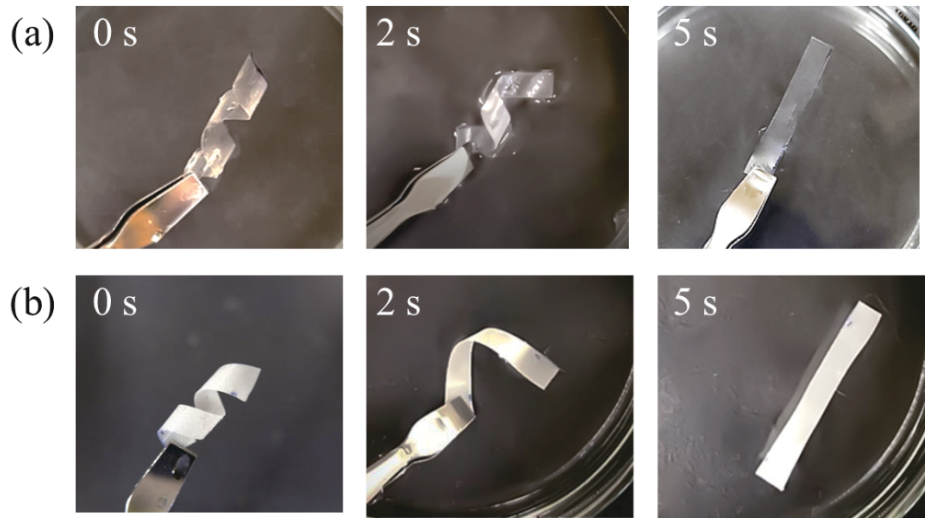

Fig.3-3 Snapshots of the shape recovery of a) SMP and b) SMP-1DBA

The shape memory behavior of the SMP samples with and without DBA were investigated, as shown in Fig 3-3. The temporary shape was deformed via heating and fixed into a spiral shape at low temperature for 5 min. The heat activation was fast and took about 5 s, so these tests were carried out using a video camera to record the recovery process of SMP gel. The SMP sample gradually recovered after placing the sample in hot water for 2 s, and it completely recovered back to the original rectangular shape within 5 s. The SMP-1DBA sample was investigated under the same conditions (see Fig. 3-3b). The recoverability of the SMP-1DBA shape was much quicker and it almost fully recovered in 2 s. By video observation, it could be seen that both samples fully recovered in 5 s and we believe that sample with DBA has the faster recovery. However, the measurement of shape memory ratio would carry out in thermomechanical analysis (section 3.3.1.2)

3.3.1.2 Shape memory effect

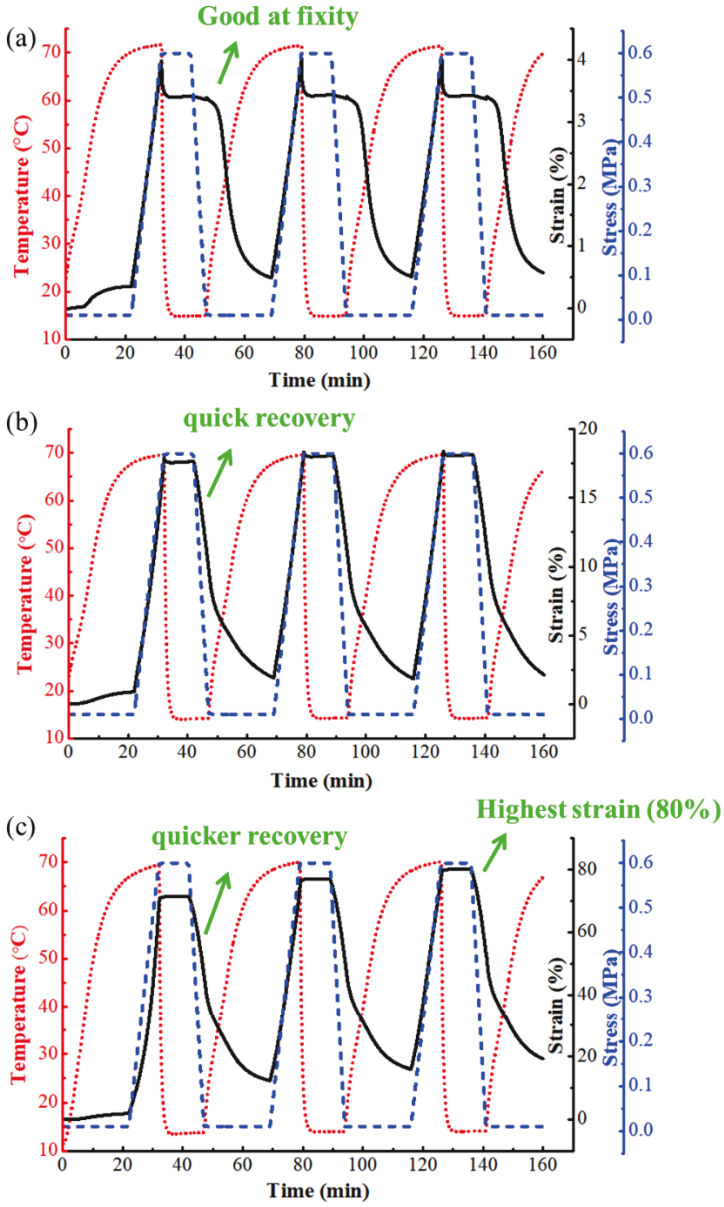

Fig. 3-4 Thermomechanical analysis of a) SMP, b) SMP-1DBA, and c) SMP-2DBA

Table 3-2 The shape recovery and shape fixity ratios of the SMP and SMP gels

Sample	Shape recovery (%)			Shape fixity (%)		
	1st cycle	2nd cycle	3rd cycle	1st cycle	2nd cycle	3rd cycle
SMP	96.12	99.46	98.11	79.00	80.49	81.64
SMP-1DBA	94.03	99.57	98.27	46.73	52.02	51.80
SMP-2DBA	84.97	94.43	94.82	48.93	53.76	52.61

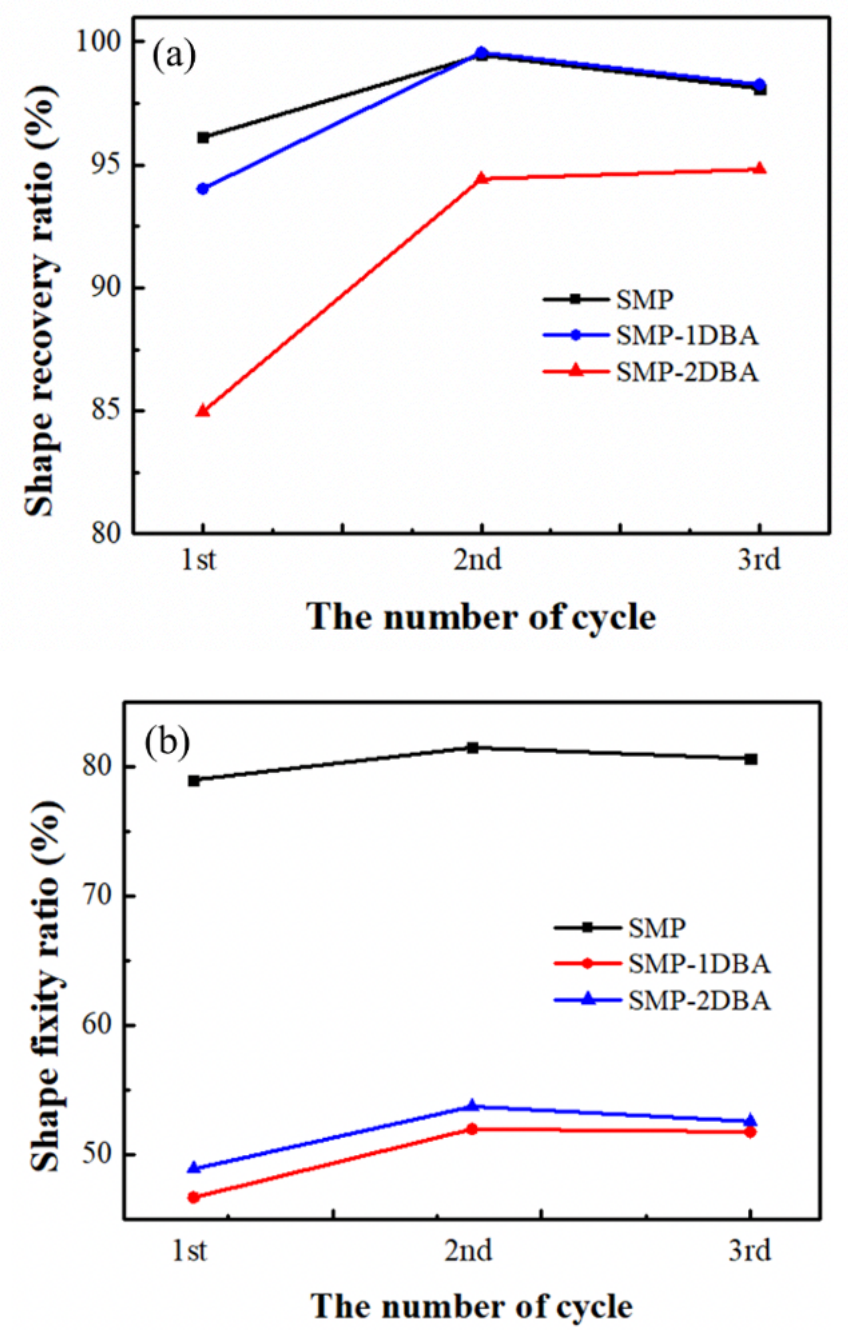

Fig. 3-5 a) The shape recovery ratio and b) shape fixity ratios of the SMP, SMP-1DBA, and SMP-2DBA gels as a function of the number of cycles

The results of the thermomechanical analysis are presented in Fig. 3-4. Three kinds of samples were selected to investigate the influence of the plasticizer on the SMP properties. The system was programmed according to the thermal and stress parameters outlined in Table 1. The shape memory recovery and shape fixity ratio were calculated from equations (3-2) and (3-3). The pure SMP was heated form the initial shape and the applied stress was gradually increased up to 0.6 MPa, as shown in Fig. 3-4a. This resulted in a change of its temporary shape

with a strain of nearly 4%. The maximum strain slightly dropped during the rapid cooling process because of stress relaxation. The temporary shape was fixed for 10 min while the temperature decreased. When the applied stress was removed, the SMP was able to maintain its shape with a shape fixity of 79%. After re-heating, the SMP gradually recovered to its original shape with a shape recovery ratio of 96%. The SMP-1DBA and SMP-2DBA gels were then tested under the same conditions (Fig. 3-4b and c). Compared with pure SMP at the same number cycles, the strain in the SMP-1DBA and SMP-2DBA gels reached approximately 18% and 71%, respectively. The strain in the SMP-2DBA sample increased to higher strain range to 76% and 80% at 2^{nd} and 3^{rd} cycles, respectively. This could be attributed to the diffusion of the plasticizer, which affected to soft segment. The plastic deformation increased alongside the increasing temperature. Besides, the shape of the SMP-1DBA and SMP-2DBA samples could be recovered after removing the stress for 6 min (same time with pure SMP); this was much faster than for the pure SMP, which had much lower strain. However, it was quite difficult to maintain the shape of the SMP-1DBA and SMP-2DBA samples after removing the stress, unlike the pure SMP, which had a good shape fixity. The addition of plasticizers resulted in a lower shape fixity of the SMP gels. The ability of the SMP gels for shape recovery and their fixity behavior were measured, as shown in Fig.3-5. The relationship between R_r and R_f with the number of cycles is shown in Table 3-2. The shape recovery ratios of all the samples were very high (up to 99%). In the first cycle, the shape recovery ratio of the SMP was 96%, and it decreased with increasing DBA plasticizer content however the shape recovery ratio increased for the 2^{nd} cycle and tended to a constant value after repeating more cycles. It indicated that the tends of values would not lower than 1^{st} cycle. This could be attributed to a reduction of memory stress and an enhanced shape memory training effect with repeated cycling of the shape [22-23]. Hence, the samples were able to easily recover after the 1^{st} cycle. Furthermore, the plasticized samples resulted in increased volume and mobility of the polymer matrix, resulting in higher strain, higher shape recovery, and lower shape fixity. The shape memory behavior of the SMP materials involves both hard and soft segments. The hard segments are crystalline and control the shape fixity. The addition of a plasticizer resulted in the formation of gels with more soft segments, which improved the shape recovery effect. The soft actuator features of these materials were expected to enhance flexibility and afford faster recovery of the original shape.

3.3.3 Electric actuation

3.3.3.1 Two-way shape deformation

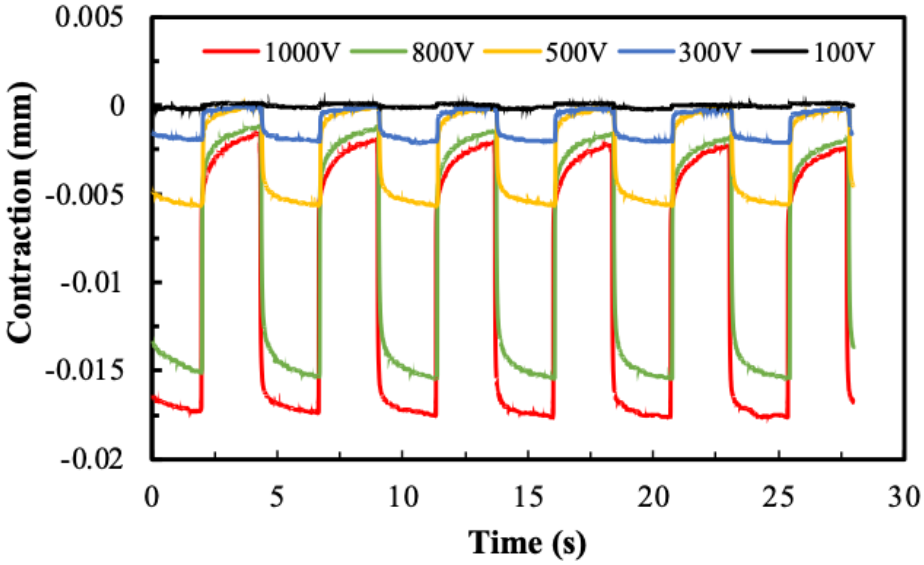

Fig. 3-6 Contraction of the SMP-2DBA gel under different applied voltages at a frequency of 0.07 Hz

The SMP-2DBA gel actuator was composed of the active material sandwiched between two conductive electrodes, which are mesh anode and a foil cathode, as shown in Fig. 3-6. The electromechanical performance was investigated in the applied voltage range of 100–1000 V. We decided to use the lowest frequency of our electric source, which might be like human body motion. The contraction and expansion of the gel actuator could be attributed to creep deformation of the gel. On application of a DC field, creep deformation of the gel occurred toward the anode side and the gel entered the mesh holes. The negative dipole of the DBA molecule caused it to move to the anode, which resulted in shrinkage and the resulting deformation was expressed as a reduction of the thickness. On switching off the applied voltage, the gel rapidly returned to its original shape. Figure 3-6 shows the contraction in thickness direction of the SMP-2DBA. The contraction was 0.18 mm at 1000 V. For this gel, a largest gap in the deformation occurred when the applied voltage was between 500 to 800 V, which was increased about 0.010 mm. This clarified that applying voltage until 800 V might be good enough to get electric actuation. Generally, the activation with lower applied voltage is preferable, safe and to save electric energy. This gel actuator showed reversibility under

repeated on-off cycling with a switching time of 2 s. Moreover, contraction occurred rapidly, and this displacement could be maintained. The actuation performance was tested over 6 cycles and showed good repeatability. The observed two-way shape deformation can be explained theoretically via the principles of electrostriction and Maxwell stress. Two types of force are primarily responsible for the deformation: one is the contraction force caused by switching the electric field on, following by the Maxwell stress; the other is the self-recovery force, which is because of expansion after switching off of the electric field, and the direction of electron motion changes, resulting in a recovery of the original shape. The results indicate that the SMP-2DBA gel had good shape recovery under an applied electric field with good cyclability.

3.3.3.2 Influence of electric field on contraction strain

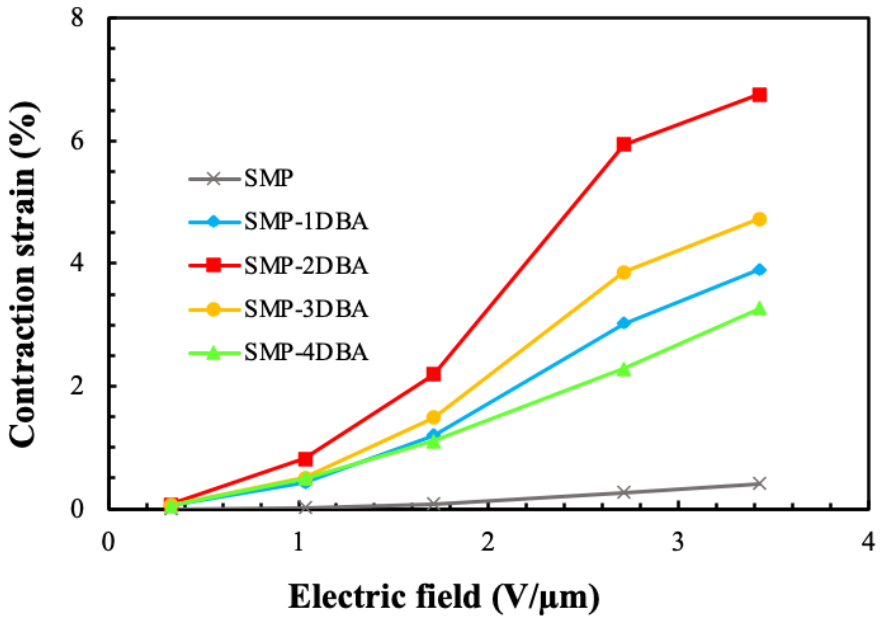

Fig. 3-7 Contraction strain of the SMP and SMP gels with different electric field intensities

Table 3-3 Dependence of the contraction strain of the SMP gels on the electric field

	Electric field(V/μm)				
Sample	0.34	1.03	1.71	2.74	3.42
SMP	0.00	0.01	0.08	0.27	0.41
SMP-1DBA	0.05	0.42	1.19	3.02	3.89
SMP-2DBA	0.07	0.81	2.19	5.94	6.76
SMP-3DBA	0.05	0.50	1.49	3.86	4.72
SMP-4DBA	0.04	0.49	1.10	2.29	3.27

The different kinds of SMP gel were tested in these electric actuation experiments, they were compared in the same stage, using the electric intensity as defined in formula (3-4) and the lowest frequency of electric source to see the movement actuation clearly. The contraction strain is shown in Fig. 3-7 and listed in Table 3-3. When the pure SMP was stimulated by electric field, only a very small contraction occurred, the displacement did not vary significantly even as the electric field increased. For the SMP gels, there was very little contraction at a low electric field of 0.34 V/μm, but increasing contraction was observed as the electric intensity increased. Under the electric intensity between 1.71 to 2.74 V/um, the contractions of SMP gels were remarkably raised and they were increase from 1.19-3.75%. Compared with other SMP gels, SMP-2DBA could be driven with large increasing contraction of 3.75%, which had the highest contraction strain of 6.76% (34.24 V/μm) The addition of a large amount of 2 times of enhanced the contraction strain about 16 times compared with pure SMP at 34.24 V/μm. The contraction slightly increased above an electric field of 2.74 V/μm. It indicated that the most suitable range of electric field to have major gab contraction is between 1.71-2.74 V/ μm. Hence, it can be concluded that the plasticized SMP contributed to an increase of the contraction strain in all the SMP gels. This was because the electrodes caused the conductive material to charge inside the active materials, and the electrons could readily migrate between the electrodes. SMP-2DBA shows the strongest ability to charge on every intensity of electric field. Referred to Maxwell stress effect, which caused by reduction of small young's modulus and increasing of dielectric constant. While the electric field activated SMP-4DBA samples, which had smallest young's modulus (experiment in the chapter 2), but the small resulting contraction strain appeared. This may be influence of plasticizers on dielectric constant is different and it is difficult for materials that are too soft to move into the mesh hole electrode, which may result in expanded deformation in the planar direction.

3.3.4 Chemical structure characterization

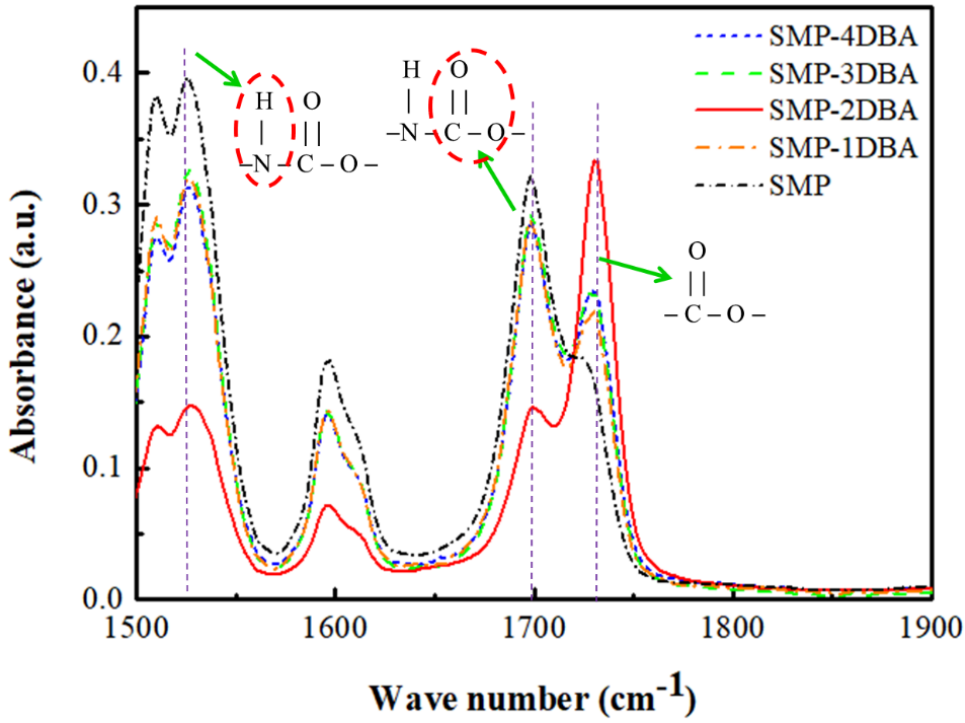

Fig. 3-8 FTIR spectra of the pure SMP and SMP gels

The chemical structures of the SMP gels was investigated via FTIR spectroscopy to clarify the composition of the SMP polymer matrix. The effect of the plasticizers on the SMP gels with different DBA contents is compared in Fig. 3-8. The pure SMP showed intense peaks that could be attributed to the stretching vibrations of C=O at 1700 cm^{-1} and an N-H group stretching vibration peak at 1530 cm^{-1}, which can be attributed to the urethane bond. After the addition of the DBA plasticizer, there was a weakening in the absorption peaks of the C=O and N-H stretching vibrations, corresponding to a reduction of the urethane group. Simultaneously, the strong absorption peak of C=O could be observed at 1730 cm^{-1}, which can be attributed to DBA. The absorption peaks associated with the C=O stretching vibration were shifted from 1700 to 1730 cm^{-1}. The carbonyl group on the DBA endowed important functionality to the activated SMP actuator and can be driven by the electric field. The decrease in the urethane groups after the addition of DBA can be associated with the reduced shape memory effect that was observed via thermomechanical analysis (section 3.3.1.2). Furthermore, the N-H group stretching vibration decreased, which indicated less hydrogen bonding in the SMP matrix. This indicated that the amount of hard segments in the SMP had reduced, resulting in less shape memory fixation and increased softness of the SMP gels. The optimization of the composition

with DBA resulted in an improved SMP that was a dielectric material, and the obtained gels demonstrated electric actuation. Moreover, the SMP-2DBA sample had the largest shifted C=O absorption peak at 1730 cm^{-1}. This explained SMP-2DBA has the highest dielectric constant value among the samples and it has the most sensitive electric actuation performance. Finally, DBA has been demonstrated as an excellent plasticizer for gel actuator formation because of the negative polarity of its carbonyl groups (C=O).

4. Conclusion

In this work, SMP gel actuator have been fabricated as dielectric elastomer and their shape memory property and actuation performance are investigated for soft actuator applications. The two-way deformation of contraction and expansion was successfully demonstrated, and several soft actuators were fabricated for practical use. The results indicated that the SMP-2DBA had the best contraction and their maximum displacement reached 6.76% for an electric field of 34.24 V/μm. In addition to the electric actuation, thermomechanical analysis showed a faster shape recovery response rate for the SMP gels. The developed SMP gels were very flexible and could be stretched up to a high strain of 80% and then rapidly recover back to their original form. Modification by the DBA plasticizers was hypothesized to cause electric polarization in the SMP gels and improve the material's properties. This was confirmed via FTIR investigation of the material's chemical structures. The SMP gel was shown to have both electric and thermal actuation. The temperature activation contributes to large and one-way shape memory deformation. Moreover, the characterizations of SMP gel actuators under electric fields are based on the principle of Maxwell stress, which show two-way shape memory effect when the electric field is ON/OFF. The use of shape memory polymers in dielectric actuators with low frequency is safer and more suitable to human body. The fabrication of SMP gel and its scale-up or down is not difficult and its flexibility is also controllable, which may endow potential uses such as medical assistance device, bandage, and artificial muscle.

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Chapter 4

SMPU tube for thermal actuation

Chapter 4 SMPU tube for thermal actuation

4.1. Introduction

SMPU have gained more attention because they have excellent unique properties that could be programmed into temporary shapes and recovered to their original shapes during thermal response. SMPU consists of two segments—the hard segments of polyisocyanate and soft segments of polyol. They are associated with the shape memory effect [1-3]. The advantage of the transition temperature (T_{trans}) contributes to the material's behavior. These features make them preferable to other materials. The polymer chains are almost frozen and good at fixing shape when $T < T_{trans}$. On the contrary, the polymer chains are easy to move when $T > T_{trans}$, affecting the shape memory recovery. Furthermore, the SMPU transition temperature ranges are controllable at 40-70 °C, which makes them suitable to be considered as biomaterials that may activate nearby human body temperature. Thermal triggering of shape-changeable materials has been used in some surgical procedures and disease treatment. Devices could be adjusted into tiny shapes that could be inserted into a small implant part and self-expand according to body temperature. In this study, we have investigated the softness of human implant-like skin to prevent discomfort during human use. The energy dissipation factor of SMPs is approximately 0.2–0.5, which is very close to the human skin values [4-6]. Therefore, its applications are being interested in the production of artificial skins. Furthermore, Young's modulus of the human skin is generally <100 MPa. This value is much lower than pure SMPU film's stiffness. The rigidity of materials may cause elastic incompatibility and undesired effects on human implants. The bio-based mechanical properties are critical for developing future medical applications integrating of understanding the mechanism via sensing and simulation training effects.

To overcome these problems, developing new composite materials with improved mechanical and shape memory behaviors for biomimetic human implants is required. Dibutyl adipate (DBA) plasticizer is a preferable alternative for fabricating gel-like soft film materials. In some studies, polyethylene glycol (PEG) was used as an additive to enhance the softness of materials but there have been reports that PEG inhibits cell activation *in vitro* [7-8]. The DBA plasticizer may increase not only the softness of materials but also biocompatibility. Previously, our laboratory group [9-13] studied and developed smart functions in soft material fields. SMPU and thermoplastic polyurethane (TPU) gels exhibit excellent potential attributed to

electric actuation because they are electroactive polymers and are expected to serve as artificial muscle [14-16] and other practical applications [17-22].

In this study, we fabricated SMP soft film-like gel materials to achieve human-like soft-part robots by incorporating DBA plasticizers. The addition of plasticizers endows the new attractive transition temperature. Furthermore, this study focused on the mechanism of mechanical properties and shape memory effect due to thermal actuation. The tensile properties are studied in different temperature conditions to investigate the influence of plasticizers on thermally induced materials, and dynamic mechanical analysis is optimized to describe the viscoelastic properties. A designed cycle programming method of thermomechanical analysis was used to explain the shape memory behavior. Particularly, to expand more practical applications, SMP tubes were fabricated and demonstrated in shape memory test of round shrinking and expanding direction by specific compression programmed method.

4.2. Experimental

4.2.1 Materials and preparation of soft films

Mixing solution was prepared using thermoplastic SMPU pellets with a glass transition temperature (Tg) of 65 °C, obtained from Diaplex SMP Technologies Inc. (Mitsubishi Heavy Industries Ltd.), and N,N-dimethylformamide (DMF) solvent, which was obtained from Sigma-Aldrich (USA). The solution ratio is 5%w/v and is mixed to dissolve within 24 h. The DBA plasticizer obtained from Wako Pure Chemical was added to the solution of SMP and DMF. To prepare the gel-like soft films, the weight ratio of SMPU to DBA plasticizers was adjusted to 1:0, 1:0.1, 1:0.3, 1:0.5, and 1:0.7 and labeled as SMP, SMP-10, SMP-30, SMP-50, and SMP-70, respectively. The mixing solution of plasticizers was mixed for 72 h and cast into a Teflon Petri dish, and the solution was evaporated at 65 °C for 5 days. Figs. 4-1a–2d shows the pure SMP and SMP gel with different content of DBA plasticizers and the SMPU gel structure images. Adding plasticizers to the SMPU component contributed to its swelling into their polymer networks, where the hard segments function as crosslinking point and soft segments function as increasing deformation, resulting in physical crosslinking gels. Their compositions exhibited softness and nontoxic human skin biomimetic properties.

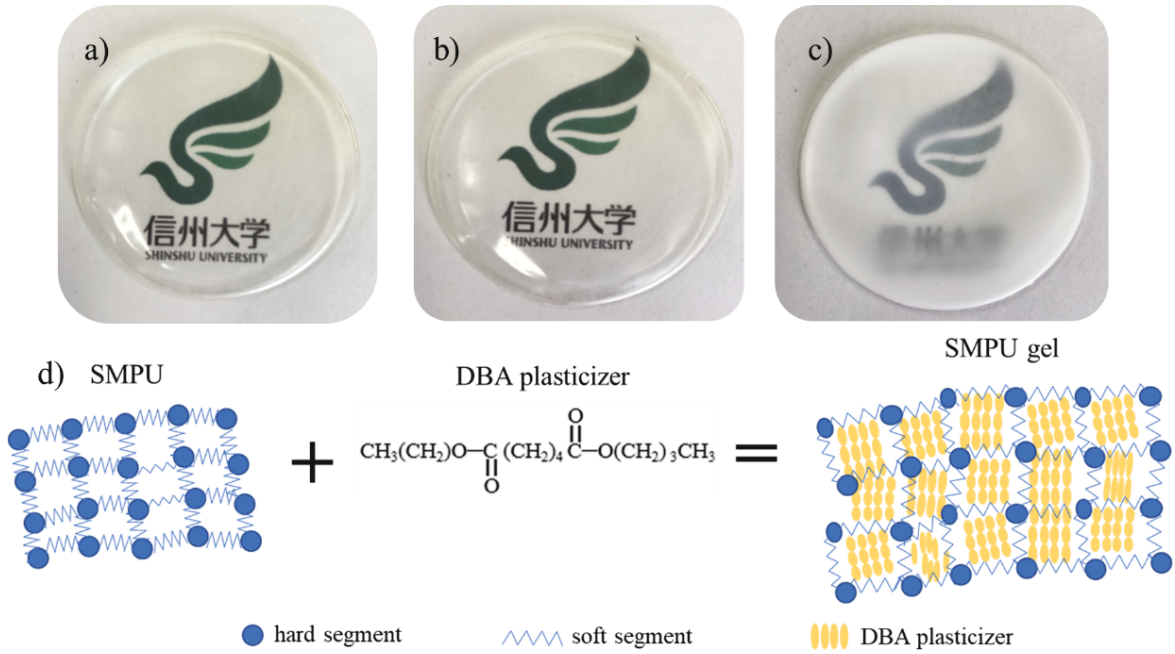


Fig. 4-1 Images of (a) S-0DBA, (b) S-10DBA, (c) S-50DBA gels, and (d) SMPU gel structures

4.2.2 Tensile property tests

Tensile property tests were conducted using a universal material tester, RTC1250A, A&D Co., Ltd., Japan. The load capacity and tensile speed were 50 N and 10 mm/min, respectively. The SMP gels with different DBA content samples were tested at different temperatures of 25 °C (room temperature), 37 °C, and 65 °C with 60% relative humidity. Each type of sample was taken 3–5 times, and the average value was used. The stress and strain were calculated with sample ‘s thickness and length.

4.2.3 Dynamic mechanical properties

The viscoelastic properties of SMP gels were analyzed by dynamic mechanical analysis (DVA-225, IT Measurement Control Co., Ltd., Japan). The samples were cut into a rectangular shape of 10 mm × 2 mm. All samples were observed with a constant heating rate of 5.0 °C/min. The oscillation frequency was 10 Hz. The samples were investigated at temperatures ranging from −20 °C to 100 °C, and the stress was measured. All samples were tested many times, and the average result was used.

4.2.4 Thermomechanical analysis

Shape memory behaviors were investigated by thermomechanical analysis (Hitachi High-Tech Science Co., Ltd. Japan) using a tensile testing method. The programs were designed and set by adjusting temperatures and stresses. First, the sample was heated to deform its shape. Second, its shape would enlarge with applied maximum stress. Then, the shape remained static at cooling temperatures; the stress was removed. Finally, it was heated again. The shape recovery and fixity ratios were calculated using the following formulas.

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)} \times 100\%, \quad (4\text{-}1)$$

$$R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m} \times 100\%, \quad (4\text{-}2)$$

where R_r represents the shape recovery ratio, R_f represents the shape fixity ratio in each cycle, ε_m represents the maximum strain at high temperatures, ε_p represents the residual strain at low temperatures, ε_u represents the strain at low stress after cooling, and N represents the number of cycles.

For the shape recovery force measurement, the samples were heated to 70 °C and the shape deformation was increased by 20%. The deformed shape was maintained for 5 min before the temperature was quickly cooled to fix its shape. The stress was adjusted to zero during cooling. The samples were heated again to 70 °C and maintained for 15 min while fixing the strain. Finally, the shape recovery force occurred and was recorded. The shape recovery stress was calculated and compared using the thickness value.

4.2.5 Tube fabrication

The gel films were cut into rectangular shapes. Teflon mandrel with a diameter of 4 mm was used to fabricate the SMP tube as shown in Fig. 4-2. To roll the cut gel sheet, it was heated at 70 °C for 2 min using hot press. The heated gel sheet was immediately wrapped to form the tube shape by rolling up the mandrel. The gel with mandrel was placed at room temperature for 5 min to fix the fabricated shape. Finally, the connecting point of the SMP tube was hot pressed again at 100 °C.

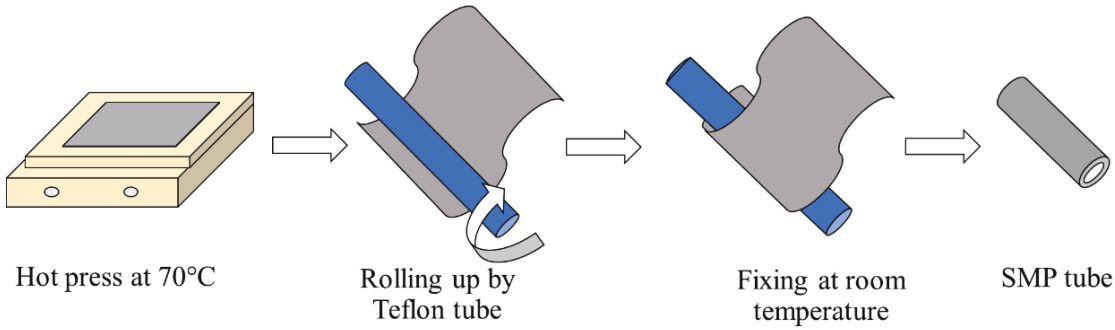


Fig. 4-2 Process of tube fabrication

4.2.6 Tube compression

Thermomechanical analysis with compression method was used to study the shape memory effect of tube compression and expansion. Tubes were set into the machine and programmed of compression with stress and temperature was applied. The fixity and recovery methods were conducted as shown in Fig. 4-3. Firstly, the tubes were heated to 70 °C, and a load was applied to the sample. The load was applied on the upper side of the tube diameter direction to achieve 10% compression in diameter direction. Then, the compressed tubes were fixed at cooling temperatures (20 °C). The recovery process was initiated simply by increasing the temperature to 70 °C. The effect of diameter change was investigated. The tube recovery ratio (T_r) was calculated using the following equation:

$$T_r = \frac{D_e}{D_c} \times 100\%, \qquad (4\text{-}3)$$

where D_e is the expansion strain on diameter direction and D_c is the compression strain on diameter direction.

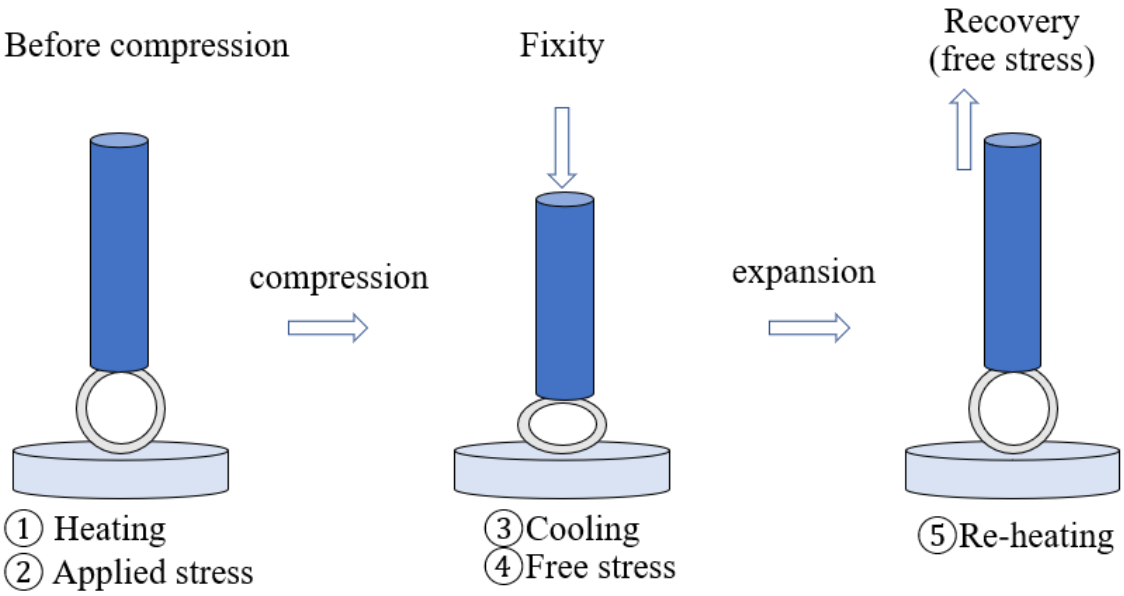


Fig. 4-3 Tube compression method by thermomechanical analysis

3. Results and discussion

3.1 Tensile properties

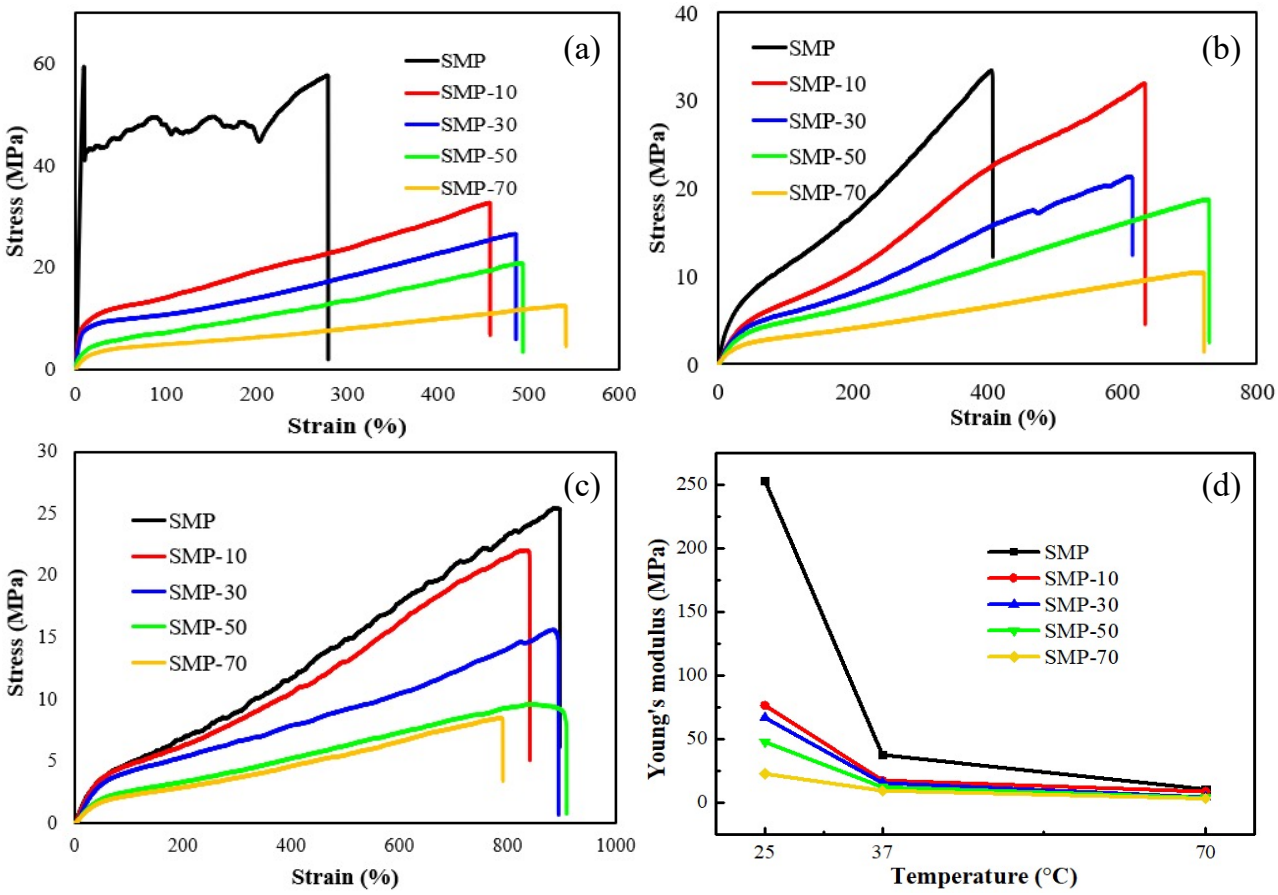


Fig. 4-4 (a)–(d) Stress-strain curves of SMP gels with different DBA plasticizer contents at room temperature (25 ℃), 37 °C, 65 °C, and Young's modulus

Table 4-1 Results of tensile properties at various temperatures

DBA Ratio	Tensile strength (MPa)			Young's Modulus (MPa)			Strain (%)		
	room	37°C	65°C	room	37°C	65°C	room	37°C	65°C
0DBA	59.52	33.39	25.39	253.16	37.86	10.88	279	408	896
10DBA	32.71	31.92	22.03	151.79	17.02	9.05	458	634	841
30DBA	26.56	21.30	15.59	73.86	14.25	4.53	486	683	994
50DBA	20.80	18.70	9.58	48.80	12.55	4.13	493	729	909
70DBA	12.50	10.42	8.48	31.72	9.75	3.62	541	721	791

Fig. 5a shows the stress–strain curve at 25 °C and the results are shown in Table 4-1. The pure SMP has high tensile strength at 59.52 MPa, and its value decreased as DBA plasticizer content increased. At 10% DBA plasticizer content, the tensile strength significantly decreased by 45% compared with pure SMP, and at DBA plasticizer contents of 30%, 50%,

and 70%, their values were slightly decreased by 55%, 65%, and 79%, respectively. Their behavior contributed to lower stiffness of materials. However, the strain value significantly increased by 64% in S-10DBA compared with pure SMP. The strain increased by 400%–541%. Their composition had more elasticity. Young's modulus describes the relationship between stress and strain as the key factor to present material softness (Fig. 4-4d). When 10% DBA plasticizer was added, the Young's modulus of the material decreased compared to when no plasticizer was added. The strain increased, which contributed to softness and stretchable of materials by adding plasticizers. This indicates that adding only 10% plasticizer content would significantly affect the softness of the gels. The samples become softer and more flexible as DBA plasticizer content increased.

The stress–strain curve at 37 °C was analyzed and showed in Fig 4-4b. The SMP gels' behaviors had changed. Young's modulus of pure SMPs was 37.86 MPa, which is close to the condition of 70% DBA plasticizer content at 25 °C. It shows that pure SMP became as soft as plasticized gels. Their Young's modulus decreased by approximately 9 times, compared with SMP-10 at room temperature. However, their tensile strength was not much different. The strain continued to elongate by >400%–729% by increasing the content of plasticizers. Their softness significantly increased at 37 °C. They not only maintained the strength of materials but also provided good elongation on their strain.

In addition, these experiments were conducted at a high temperature of 65 °C to investigate the limit of plastic deformation, as shown in Fig. 4-4c. The behavior of SMP and SMP-10 is similar to each other. Young's modulus of SMP-30 decreased by approximately 2 times compared to SMP-10, and their strain was elongated by almost 1000%. After adding over than 30% DBA, the tensile strength and Young's modulus slightly decreased. However, all samples had an extremely high elongation at 65 °C. Adding more plasticizers to SMPs increased its flexibility. However, the strain in SMP-50 and SMP-70 became smaller because their networks are weak and have less elongation to be broken. The temperature could reduce the gap between pure SMP pure and plasticized gels' behavior. These indicated that plasticizers diffused into the SMPU matrix and formed loose structures based on secondary bonding forces. Pure SMP's behavior was changed at 37 °C because their Young's modulus became less than 100 MPa, which is more suitable for fabricating human implant-like materials. We believe these SMP gels would be more comfortable for human use. This experiment could be used to simulate tensile properties to biomechanical performance at different states for use as temperature controllers.

4.3.2 Dynamic mechanical properties

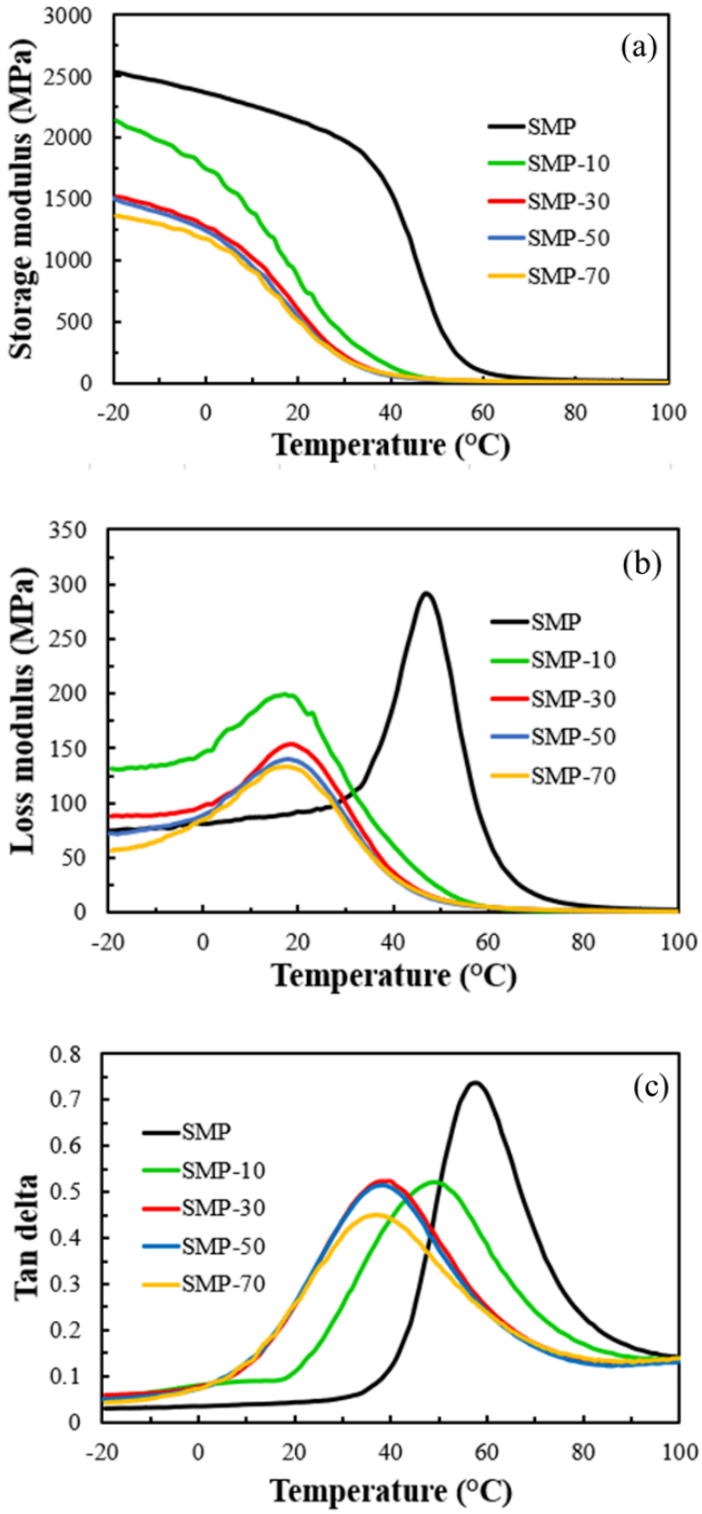


Fig. 4-5 DMA test results of (a) storage modulus, (b) loss modulus, and (c) tan delta with increasing temperatures of all SMP gel samples

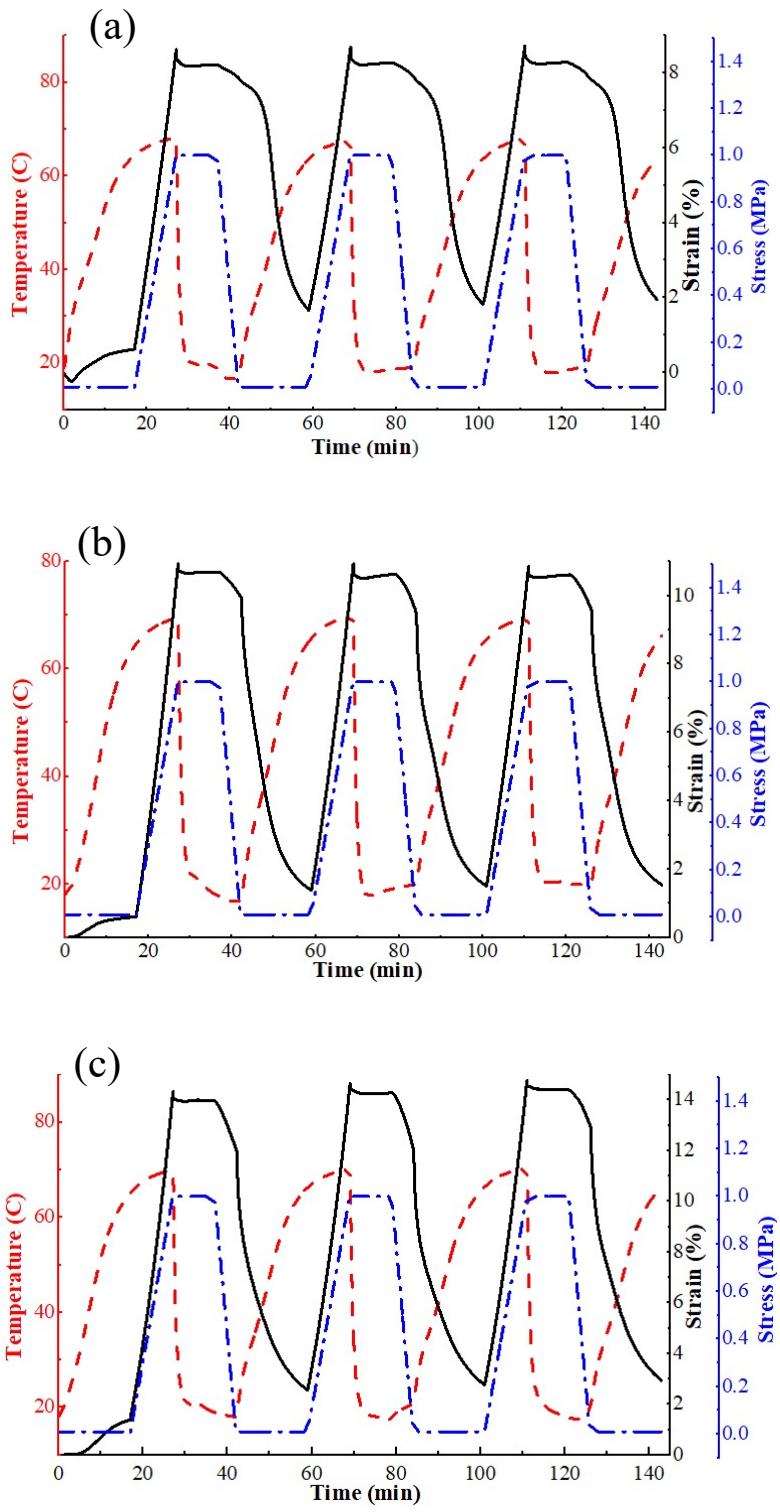
The relationship between the storage modulus, loss modulus, and loss factor tan delta will explain the influence of temperature on viscoelastic properties. The good shape memory behavior always necessitated a different status between the lower and upper the transition temperatures. All samples were investigated from −20 °C to 100 °C. At low temperatures, the glassy state modulus refers to elastic energy storage. On the contrary, a rubbery state modulus is observed at high temperatures, which implies entropy elasticity. According to Fig. 4-5a, the storage modulus of pure SMP at low temperatures is extremely high, measuring 2532 MPa. Because the materials are elastic, the storage modulus at high temperatures decreased by two orders of magnitude at high temperatures, demonstrating the shape memory function. At 10% DBA plasticizer content, the storage modulus slightly decreased. However, it significantly decreased at 30% DBA plasticizer content. The storage modulus reduced with increasing DBA plasticizer content because the soft segment increased in the SMP matrix.

The loss modulus of materials can be defined as the loss of stored energy due to changes in the polymer behavior during heating. According to Fig. 4-5b, loss modulus values decrease with increasing temperature. With increasing DBA plasticizer content in the SMP matrix, the modulus decreased and shifted backward to a lower temperature range, which represents the dissipation of strain energy in the polymer chains, leading to the shape recovery effect.

These behaviors are related to tan delta, which is the parameter ratio of the loss modulus to the storage modulus and represented in damping properties. They demonstrate the difference between two phases in polymer composites. At low temperatures, the damping factor is extremely low because the polymer chains are frozen and good for shape fixity. However, the values increased at high temperatures because the polymer chains can be easily moved. Pure SMP showed the highest damping value, which implied that they are the least elastic compared with other samples. The highest peak between the two phases was referred as the glass transition temperature (Tg) (Fig. 4-5c). The switching in the Tg range was significantly shifted to a lower temperature ranging from 60 °C to 49 °C for SMP-10 and Tg was gradually shifted to 40, 38 and 37 °C for SMP-30, SMP-50, and SMP-70, respectively. Their transition temperatures became close to human body temperature after increasing the amount of plasticizers. By changing the temperature, the glassy state was transformed into a rubber state. The developed SMP gels have low storage modulus and loss modulus, indicating that the elastic modulus of SMP gels decreased because of soft segment increment. These experiments have shown similar trends and could be supported by the tensile properties discussed in Section 4.3.1, which show that tensile strength and Young's modulus decreased with increased strain.

4.3.3 Shape memory behavior

4.3.3.1 Thermomechanical properties



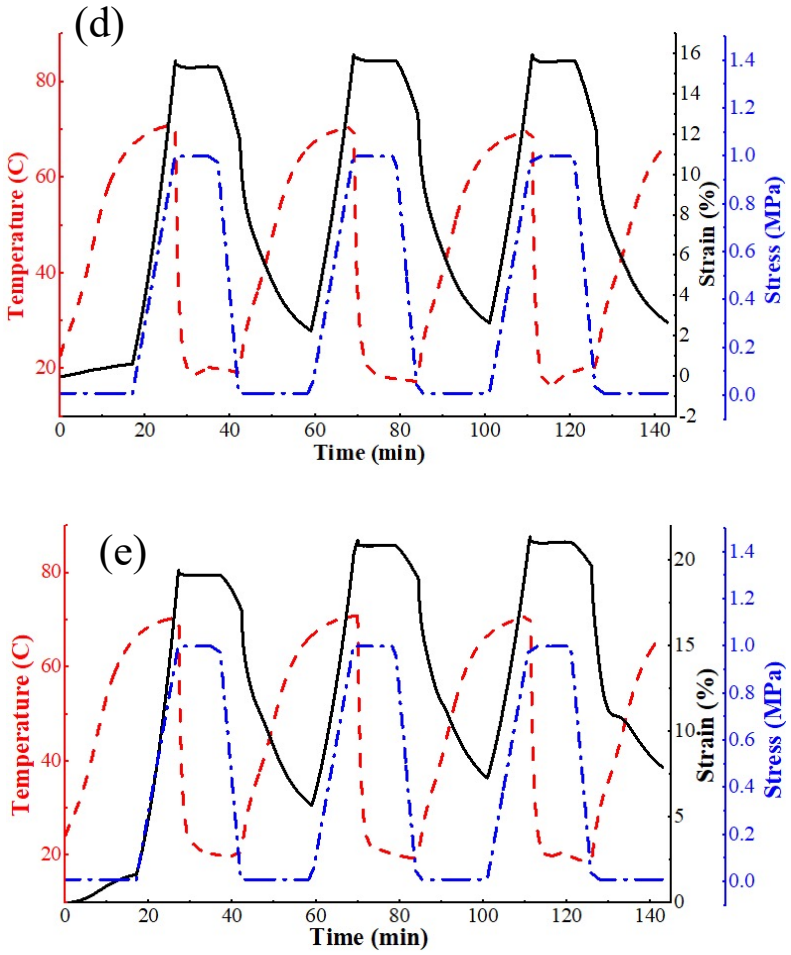


Fig. 4-6 Thermomechanical analysis on tensile deformation of (a) SMP, (b) SMP-10, (c) SMP-30, (d) SMP-50, and (e) SMP-70

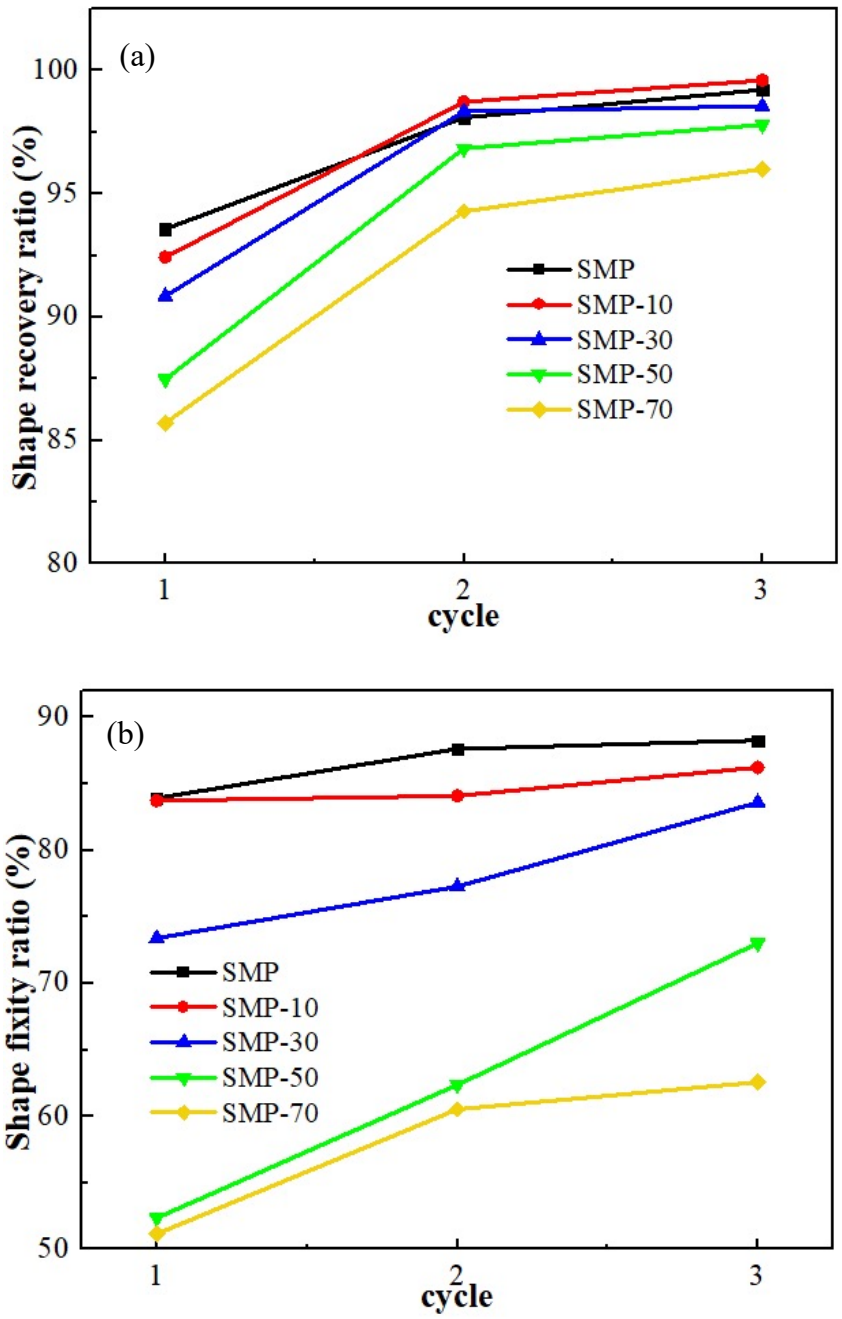


Fig. 4-7 (a) Shape recovery and (b) shape fixity ratios of SMP gels with the number of cycles

Table 4-2 Shape memory recovery and fixity ratios

Sample	Shape recovery (%)			Shape fixity (%)		
	1st cycle	2nd cycle	3rd cycle	1st cycle	2nd cycle	3rd cycle
SMP	93.57	98.09	99.22	83.93	87.63	88.27
SMP-10	92.43	98.73	99.60	83.74	84.10	86.24
SMP-30	90.85	98.34	98.55	73.40	77.28	83.60
SMP-50	87.48	96.84	97.80	52.36	62.37	73.02
SMP-70	85.71	94.29	96.00	51.16	60.53	62.57

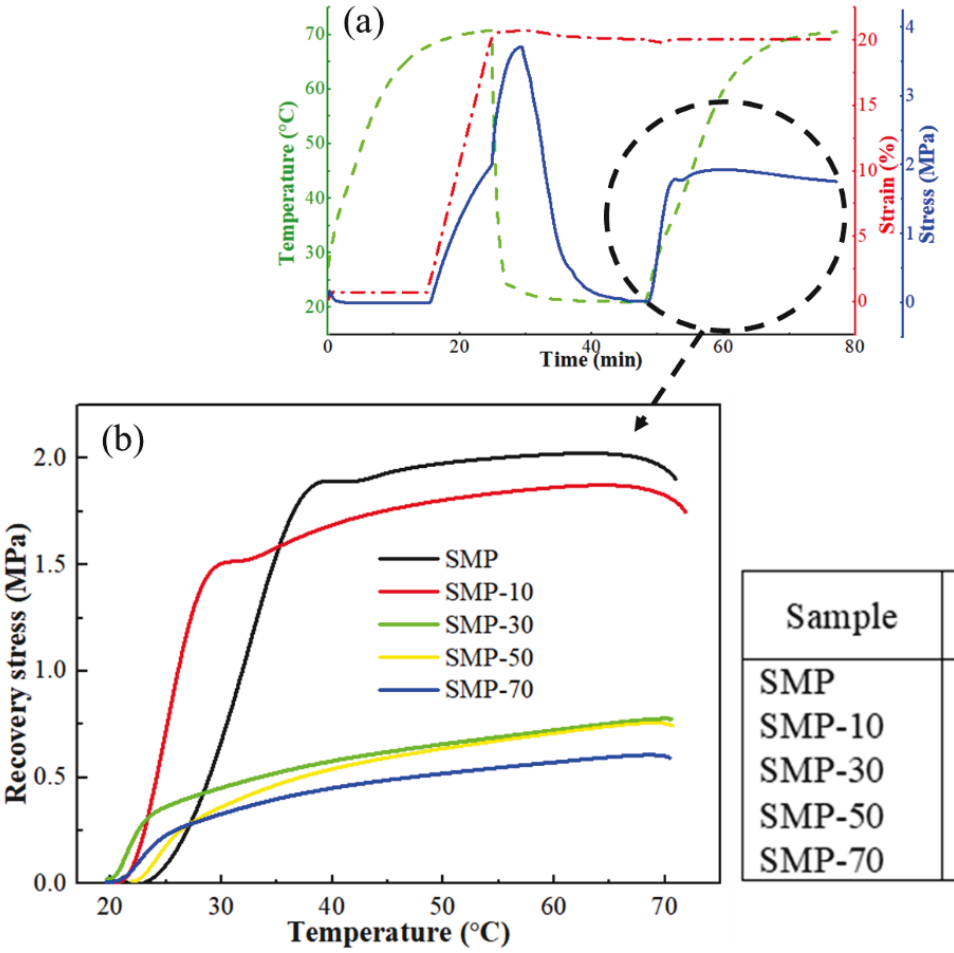
All results of the thermomechanical analysis were conducted under the temperature range of 20 °C–70 °C to investigate the shape memory behavior, as shown in Fig. 4-6. All sample types were adjusted by heat and stress programming. The shape recovery (R_r) and fixity ratios (R_f) were calculated using Equations (1) and (2), as shown in Fig. 4-7 and Table 4-2. According to Fig. 6a, S-0DBA gel was heated and stressed until 1 MPa. Its strain was stretched to approximately 4% and immediately fixed by cooling. With the same cycle, the strain was increased by approximately 10%, 14%, 16%, and 23% for SMP-10, SMP-30, SMP-50, and SMP-70, respectively (Fig. 4-6b–6e). It showed that the effect of DBA plasticizer contributing to the strain became larger when the gels were heated over their transition temperature. However, their stain was slight dropped due stress relaxation when the temperature was immediately cooled. After that, their shapes could be maintained for 10 min and the stress was gradually removed. SMP had a shape fixity of 83.93% and could recover to their original shapes at shape recovery of 93.57%. They have a good trend of shape recovery effect for all samples. However, their shape recovery became slightly lower as the plasticizer content of their composites increased. Compared with the same cycle, it showed that the shape recovery behavior of SMP-10 was not different from that of pure SMP. However, the shape fixity was slightly decreased to 90.85% and 87.48% for SMP-30 and SMP-50, respectively. At 70% DBA plasticizer content, the shape recovery was decreased to 85%.

In terms of shape fixity effect, SMP-10 behaved almost similar to SMP. However, the shape recovery fixity of SMP-30 decreased to 73.40%. SMP-50 and SMP-70 have low values of shape fixity at 52.36% and 51.16%, respectively. Because their composites contain an excessive amount of DBA plasticizer content, shape fixity has become difficult, and they have a faster recovery effect. After re-heating, their shapes immediately recovered to their original shapes.

After testing more than 1st cycle, shape memory recovery and fixity improved in the 2nd cycle. The repeated number of cycles contributed to a better shape memory effect due to its effect of memory stress reduction and shape memory training [23-25]. At higher number of cycles, the strain for SMP-70 was shifted into the higher range. A significant number of soft segments have been added to their composites, and heat elongated the deformation. SMP have soft and hard segments. Filing plasticizers into their structures, which is the same as incorporating soft segments, resulted in better shape recovery and strain but poor shape fixity. According to dynamic mechanical analysis, these composite materials may have a good shape memory effect. The storage modulus and loss modulus were also related to shape recovery and

shape fixity. At low temperatures, it results in good shape fixity while cooling. At high temperatures, the materials are in a rubbery state, which is attributed to the shape recovery effect. In this study, we chose the best shape recovery and fixity behavior to create desired applications for more practical uses as tube actuators. They are expected to be wrapped or attached to the human body to monitor triggers in temperature.

4.3.3.2 Shape recovery stress



Sample	Recovery stress (MPa)
SMP	2.02
SMP-10	1.87
SMP-30	0.78
SMP-50	0.76
SMP-70	0.60

Fig. 4-8 Shape recovery stress; (a) processing method and (b) thermomechanical analysis results

According to the programming method of thermomechanical analysis in Fig. 4-8a, the shape recovery stress of all samples was directly observed. The strain of samples increased to approximately 20% and the stress was adjusted to nearly zero during the cooling process. Further, the temperature was raised and the strain gradually recovered. The recovery stress can be observed in Fig. 4-8b. SMP and SMP-10 have better recovery stress than other samples, so they would have a good shape fixity behavior. As the amount of plasticizer increased, the recovery stress became smaller. The recovery stress of SMP-70 decreased 3.37 times as compared to SMP. The stored energy is related to recovery stress at changing temperatures. The investigation of recovery stress reveals the small values of 0.60–2.02 MPa, which is 100 times lower than metal materials. We believe that the recovery behavior of this actuator makes

it more preferable for use in thermal sensing with biomaterials and less painful, which is required for small stress.

4.3.4 Tube compression recovery

4.3.4.1 Direct heating behavior

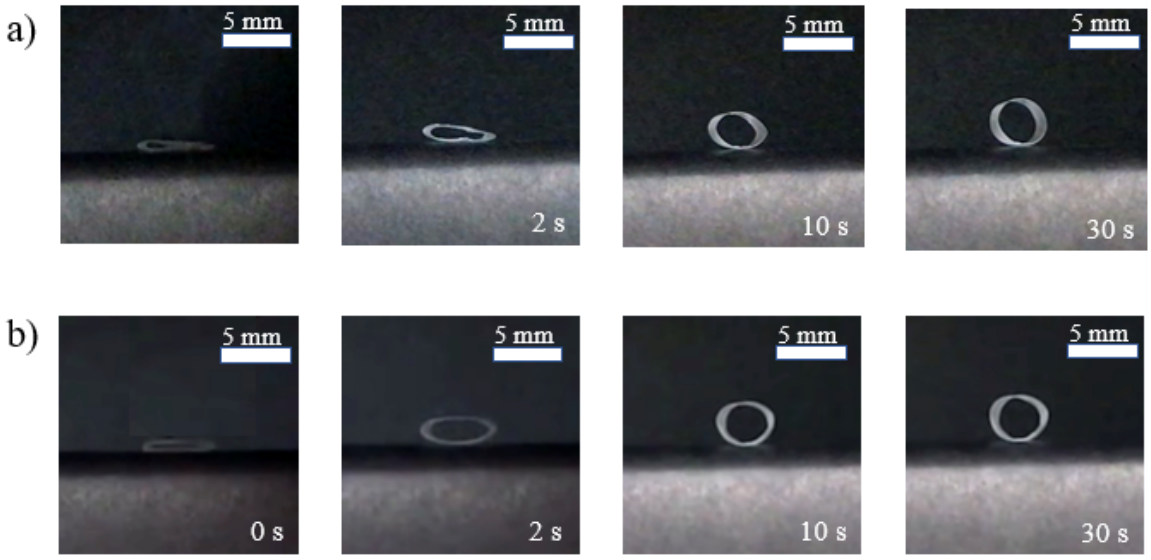


Fig. 4-9 Shape recovery behavior of compressed (a) SMP and (b) SMP-10 tubes by direct heating

The compression-induced shape memory recovery of SMP and SMP-10 tubes was observed and depicted in Fig. 4-9. The tubes were formed using a Teflon tube mandrel by heating and fixed during cooling, as shown in Fig. 4-3. Further, the SMP tube was manually hot pressed to reduce its diameter and fixed the performed shape at 10 °C. The shape recovery was performed in an oven at 40 °C by recording video camera to demonstrate the trend of the recovery effect in the state of human body temperature. From Fig. 10a, the compressed SMP tube began to recover gradually at 2 s. However, the SMP-10 tube had greater recovery effect than the pure SMP tube due to the occurrence of larger recovery. The recovery of SMP-10 was immediately occurred, and almost full recovery was reached within 10 s (Fig. 4-9b). The SMP and SMP-10 tubes exhibited fast recovery results on compression and full recovery less than 30 s was observed.

4.3.4.2 Compression recovery by thermomechanical analysis

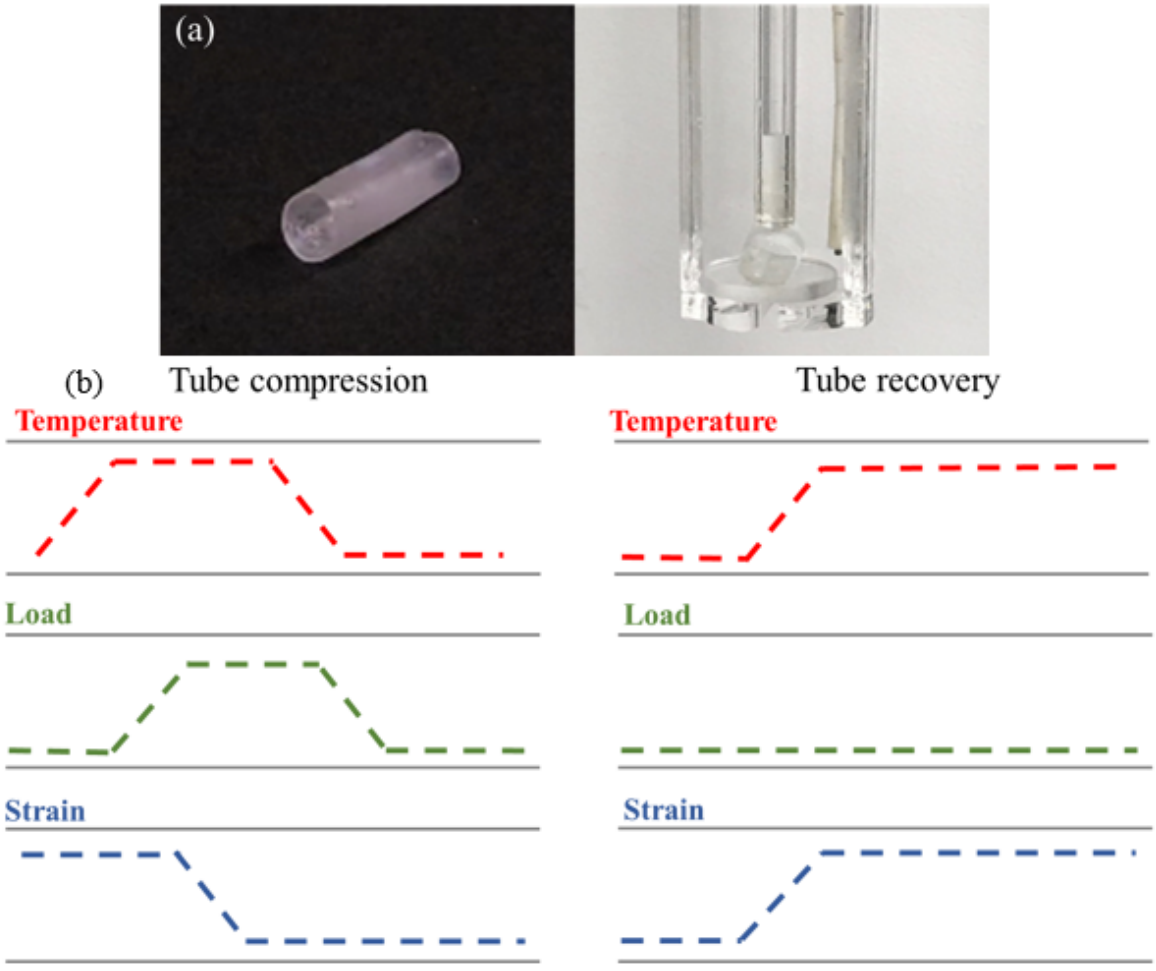


Fig. 4-10 (a) SMP tube and (b) tube compression process of the temperature–load–strain curve by thermomechanical analysis

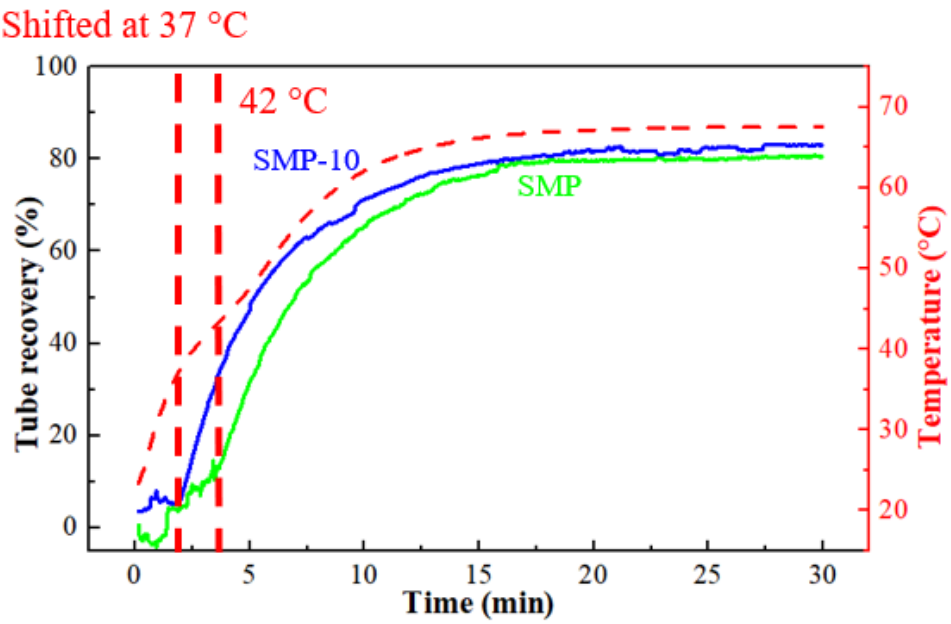


Fig. 4-11 Shape recovery ratio of tube compression on thermomechanical analysis

One of the most popular processing shapes for producing smart devices for biomaterials is the tube actuator, which can activate in round shrinking and expansion forms via diameter direction. Through thermomechanical analysis, tube compression process can be performed, as shown in Fig, 4-10, to observe tube recovery ratio. We have chosen two types of gels (SMP and SMP-10) with excellent shape memory effect behavior to test tube compression deformation. The machine probe compressed the tube up to 10% in the diameter direction (Fig. 4-3), and the recovery process was conducted by simply increasing the temperature. Fig. 11 shows the tube recovery ratios of SMP and SMP-10 tubes. Only heating and freeloading were used in the recovery process. The heating rate increased from a 20 °C to 70 °C within 20 min, and the heating rate became stable. The significant change in the recovery ratio of the SMP tube occurred at 42 °C, whereas the change for SMP-10 occurred at 37 °C. Furthermore, they both exhibited similar performance to reach the maximum recovery. The SMP tube had a maximum recovery ratio of 79%, whereas that of the SMP-10 tube was 83%. This shows that adding DBA plasticizer into SMP composites produce a faster shape recovery effect than pure SMP, which is a similar trend observed in the tensile deformation test of the shape memory effect. In addition, large turning point occurred at lower temperature, contributing to their switching temperature range being closer to the human body temperature.

4.4 Conclusions

In this study, a shape memory tube was successfully fabricated using SMP–DBA composites as a thermal responsive actuator, and their mechanical properties, shape memory properties, and biocompatibility were optimized for biomaterial applications. Their softness was adjusted to be close to the softness of human implants, and temperature stimuli contributed to a great elongation of up to 900% by plastic deformation. Particularly, the glass transition temperature was controlled and significantly lowered from 60 °C to 37 °C, which is close to the range of human body temperature. Tensile deformation increased the shape recovery effect of SMP gels up to 99%. The tube compression and expansion demonstrated tube recovery in the diameter direction up to 83% for SMP-10 gel, and their large recovery behavior started from 37 °C. This shows that DBA plasticizer-doped SMPs have a faster shape recovery rate at lower temperatures than pure SMP. Furthermore, DBA plasticizer-doped SMP has a maximum small recovery stress of 2.06 MPa, which showed that they are safe for use in the human body. In addition, the cell adhesions and proliferation of NH3T3 mouse cells demonstrate that these SMP gel and its tube actuators can be used in the human body, which has aided our work on drug release systems for biomedical applications. In the future, SMPU–DBA gels are also expected to be used in producing thermal tube actuators for drug delivery, artificial blood vessels, and other aspects of tissue engineering.

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Chapter 5

SMPU tube for electric actuation

Chapter 5 SMPU tube for electric actuation

1. Introduction

Recently, the development of smart materials involved multiple research fields worldwide, including physics, chemistry, computer science, applied science, and engineering. The study of composite materials and their structure contributes to the wide applications of smart materials. Smart materials have been successfully used in applications, and research on the development of optimized stimuli-responsive materials is increasing [1-3]. Among multiple responsive materials, shape memory polymer is the most interesting study for wide applications such as deployment structure and high-performance sensors [4-5]. Remarkably, they have the potential properties to develop for biomedical uses such as implant devices, stents, vascular and artificial muscle [6-10].

Generally, shape memory polyurethane (SMPU) has excellent performance on thermal actuation since its behavior could be adjusted by taking advantage of the glass transition temperature. Polyurethane composites were controlled their shape memory effect by transition temperature control [11-12]. They consist of two segments: the hard segment from the isocyanate group and the soft segments from the polyol group, which played the role of fixity and recovery state [13-14]. However, SMPU is an insulator material. To extend their ability, the idea of a dielectric elastomer actuator was used to integrate with SMPU materials. Adding dielectric filler is a favorable choice to overcome this issue. Polymer plasticizer addition can create gel-like soft film materials because they diffuse into the polymer molecule and increase the SMPU matrix's free volume. This interaction results in softer materials. Additionally, some studies [15-16] have compared the use of DBA with other plasticizers such as dioctyl adipate (DOA). The DBA structures consisted of smaller diester molecules, and it was found that its molecular weight was more desirable for soft actuator applications. Especially, DBA has tested non-toxicity for human body implant [17]. Research in our laboratory also studied polyurethane actuators with DBA plasticizers because of the increased environmental friendliness of polyurethane, and it confirmed the possibility of replacing PVC, which might not be safe for human body use [18-19]. Moreover, SMPU has thermal activation ability, which is difficult for TPU [20-21]. However, the dielectric properties of SMPU and DBA composites are limited, so the other filler adding will be applied to this composite.

Currently, biodegradable and sustainable materials are considered as an alternative way to address the environmental problem. However, the most commonly used dielectric elastomer

actuators mainly are non-biodegradable and non-renewable materials, such as polyethylene terephthalate (PET), polypropylene (PP), polyethylene naphthalate (PEN), polyphenylene sulfide (PPS), polytetrafluoroethylene (PTFE), and polystyrene (PS) [22-25]. Recently, cellulose-based biodegradable materials have been highly interested in developing responsive functional materials such as bacterial nanocellulose (BNC), cellulose nanofibril (CNF), cellulose nanocrystal (CNC). Since they have several advantages, such as improving mechanical properties, barrier membranes, water absorption, and dielectric properties [26-29].

For our study, the use of cellulose nanocrystals (CNC) with SMPU-DBA matrix is expected to enhance the dielectric properties of SMPU. CNC is short particles with the length of micro to the nanoscale [30-31]. Its composites have been studied, and its applications are mostly developed for tissue engineering [32-33]. Since CNC consists of cellulose molecules, which have the rich phase of hydroxy groups and carbonyl groups. For example, Bonardd's group [34] reported that the addition of CNC into chitosan enhances dielectric constant and Ram et al. [35] studied that polyvinylidene fluoride/CNC composite have an improvement of dielectric induce. These components would support SMPU matrix easy to stimulate the polar groups. The study on the electromechanical performance of SMPU composites is followed by the principle of Maxwell's stress [36].

$$S_z = -\varepsilon_0\varepsilon(V/Z)^2/Y, \qquad (5\text{-}1),$$

where Young's modulus (Y) and dielectric constant (ε) are the main keys to achieve high performance of dielectric elastomer actuator. When an electric field was applied to the polymer and electrode, it results in deformation. Some research showed that incorporating CNC into polymer matrix could obtain the higher dielectric constant value. CNC enhances their dielectric properties [37-38], which functions to control the displacement and is an essential key for obtaining tube contraction and expansion on electromechanical performance. This is challenging work to develop an electric stimuli-responsive for the green-material tube. Moreover, all components are friendly to the human body and environment. which is also expected for use in the bioengineering field.

In this chapter, we proposed the improvement of the dielectric SMPU gel actuator by using the alternative filler of CNC and focusing on the mechanical properties. Its designed tube was fabricated and investigated its tube contraction and expansion deformation on electric actuation. The chemical composition was investigated to clarify the material's behavior and support the

actuators on electric actuation. The results of this work would present a foundation for further work on SMPU soft materials and their potential application for bio-green actuators.

5.2. Experiment

5.2.1 Preparation of SMPU/DBA/CNC gels

The mixing solution was prepared using thermoplastic SMPU pellets with a glass transition temperature (Tg) of 65 °C, obtained from Diaplex SMP Technologies Inc. (Mitsubishi Heavy Industries Ltd.), and N,N-dimethylformamide (DMF) solvent, which was obtained from Sigma-Aldrich (USA). The CNC was derived by chemical hydrolysis using a strong acid such as H2SO4 solution [28]. The solution ratio is 5%w/v and is mixed to dissolve within 24 h. The DBA plasticizer obtained from Wako Pure Chemical was added to the solution of SMP and DMF. The weight ratio of SMPU to CNC plasticizers was adjusted to 1:0, 1:0.1, 1:0.3, 1:0.5, and 1:1.0 and labeled as 0CNC, 1CNC, 3CNC, 5CNC, and 10CNC, respectively. To prepare the gel-like soft films, 2: 1 of DBA to SMPU was added to all SMPU/CNC solutions. The mixing solution of plasticizers was mixed for 24 h and cast into a Teflon Petri dish, and the solution was evaporated at 65 °C for three days. Fig. 5-1 shows the pure SMPU and SMPU/DBA and SMPU/DBA/CNC gel images. Adding CNC to the SMPU/DBA component contributed to the hard segments function as crosslinking point and adding DBA plasticizer to its matrix contributed to the soft segment. Their gel changed from transparent to white color by adding CNC.

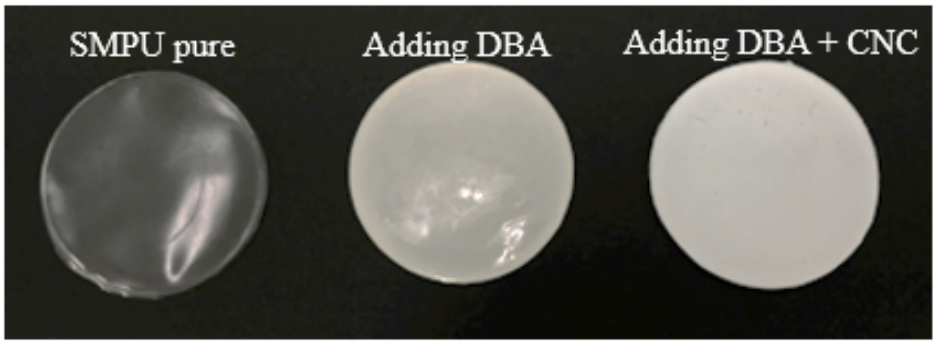

Fig. 5-1 Images of (a) SMPU pure, (b) 0CNC, and (c) 5CNC

5.2.2 Dynamic mechanical properties

The viscoelastic properties of SMP gels were analyzed by dynamic mechanical analysis (DVA-225, IT Measurement Control Co., Ltd., Japan). The samples were cut into a rectangular shape of 15 mm × 5 mm. All samples were observed with a constant heating rate of 5.0 °C/min. The oscillation frequency was 10 Hz. The samples were investigated at temperatures ranging from −20 °C to 100 °C, and the stress was measured. All samples were tested many times, and the average result was used.

5.2.3 Impedance analysis

The interaction between the polymer and plasticizer behavior was investigated using an impedance analyzer, Solartron 1260/1296, Toyo Technical Ltd., Japan. The samples were cut into circles with a diameter of 14 mm. The experiments were carried out in the frequency range of 100–106 Hz at 100 mV. Each type of sample was tested three times, and the average value was used. The dielectric constant (ε) and charge storage capacity increased, but the interfacial resistance decreased with increasing CNC content in the samples. This could be calculated by the below equation.

$$C_0 = \varepsilon_0 \times A/d, \qquad (5\text{-}2),$$

where C is the capacitance, A is the conductive area, and d is the distance between the conductors.

5.2.4 Tube fabrication

The 5CNC gel was cut into rectangular shapes. A stainless mandrel with a diameter of 5 mm was used to fabricate the tube. To roll the cut gel sheet, it was heated at 70 °C for 2 min using hot pressing. The heated gel sheet was immediately wrapped to form the tube shape by rolling up the mandrel. The gel with mandrel was placed at room temperature for 5 min to fix the fabricated shape. Finally, the connecting point of the SMPU tube was hot-pressed again at 150 °C.

5.2.5 Electric response

The gel samples were cut into rectangles with dimensions 20 x 20 mm. The gel actuator was prepared by sandwiching the active gels/tube between the metal electrodes. An electrical charge was applied from the foil cathode into the gel; the electrons migrated toward the stainless mesh anode through the SMP gel. The surface properties of the gel allowed for facile stacking with the electrodes. The displacement was observed in the thickness direction using a laser displacement meter LK-G3000, Keyence Co., Japan. The test was performed at 0.1 Hz and recorded for 60 s. The SMPU gel was tested in 500–1500 mV to study the actuation performance.

The SMPU tube was used and placed between two metal electrodes, and the electric source was applied from the bottom to above of tube, resulting in the deformation in the diameter direction. The following equation calculates the % contraction.

$$\% \, C = \frac{d}{D} X100 \qquad (5—3),$$

Where C is % tube contraction, d is deformation, and D is the original diameter of the tube.

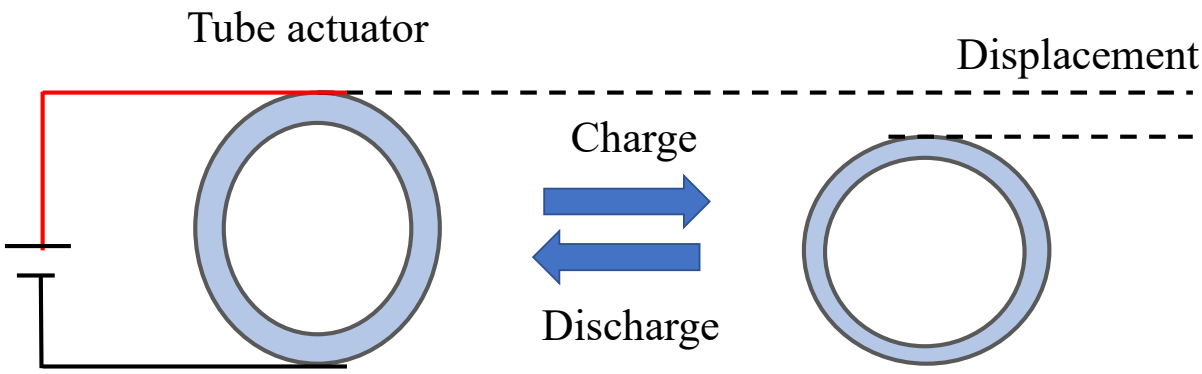

Fig. 5-2 Image of tube deformation during electric charging and discharging

5.2.6 Fourier-transform infrared spectroscopy (FTIR)

The chemical structures of the SMPU/DBA/CNC composites were investigated via FTIR, Shimadzu IR Prestige-21, Japan. The FTIR spectra of the thin films were analyzed in the range 500–4000 cm^{-1} at room temperature.

5.3 Results and discussion

5.3.1 Tensile properties

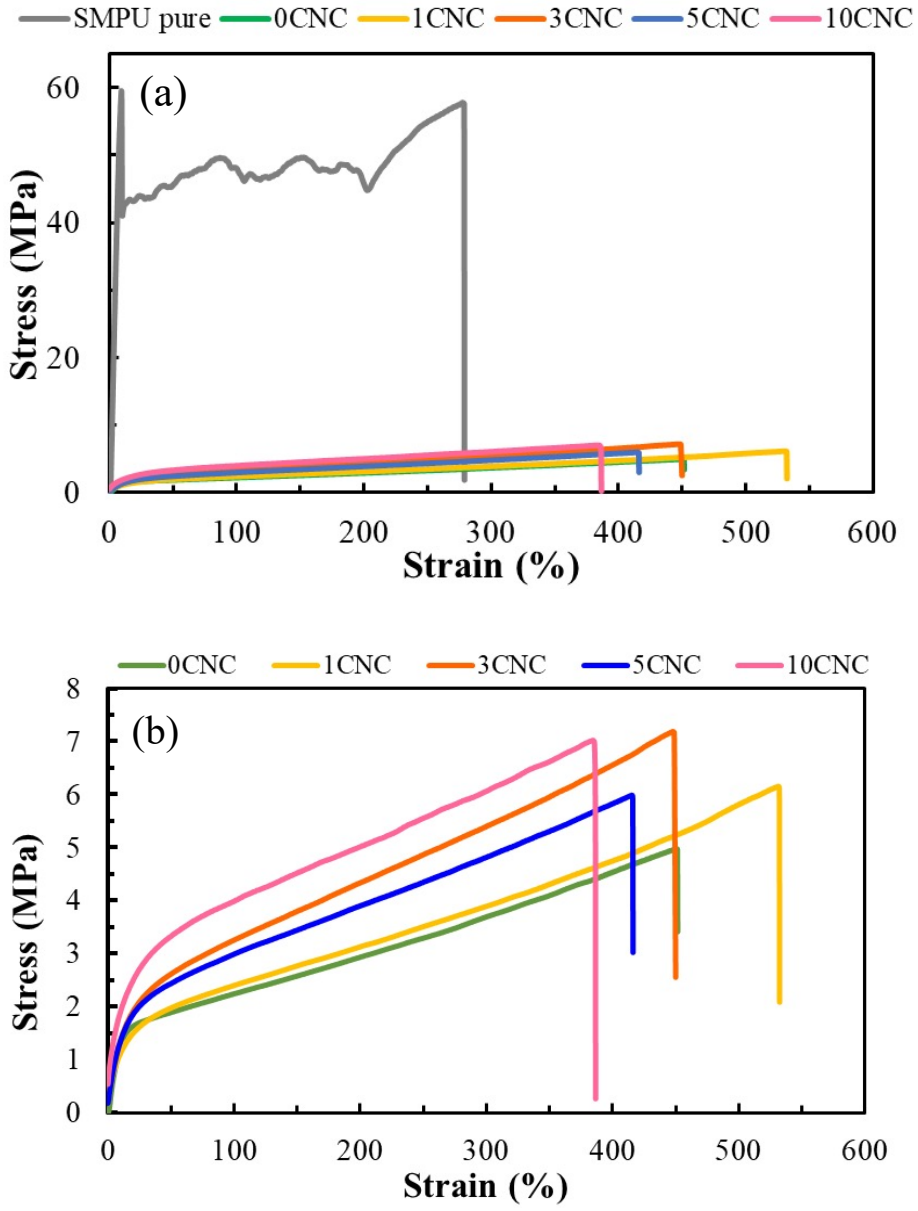

Fig. 5-3 a) Stress-strain curve of SMPU gel and b) SMPU gel with different content of CNC

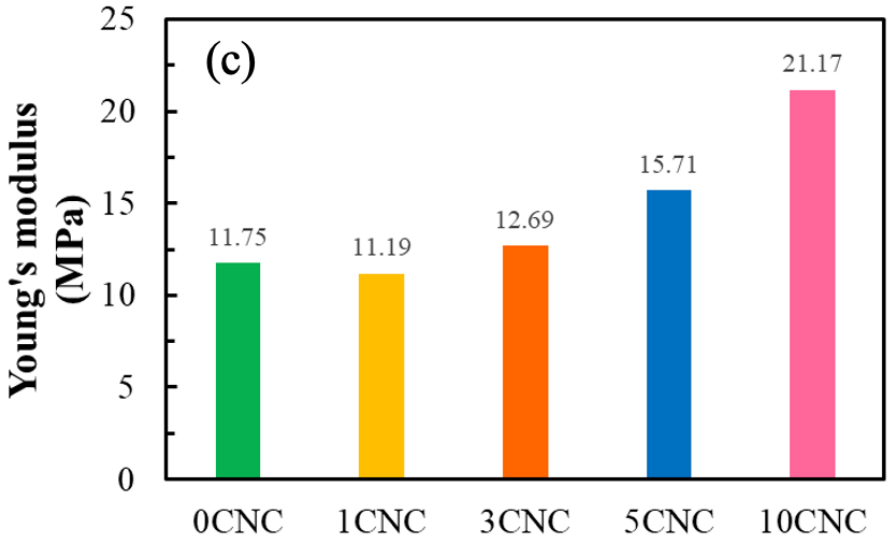

Fig. 5-4 Initial young's modulus values at of SMPU gels and SMPU gels with different content of CNC

The stress-strain curve of the pure SMPU and the SMPU gels are shown in Fig. 5-4a. The pure SMPU sample has a very high tensile strength at break of 57.59 MPa. The SMPU incorporated with DBA plasticizers sample (0CNC) presents a significantly lower tensile strength than pure SMPU. After adding CNC to SMPU gels, the tensile strength was slightly increased by about 1-2 MPa, compared with 0CNC (see Fig.5-4b). The initial Young's modulus exhibits the relationship between stress and strain, which is the main factor for developing a soft dielectric actuator. From Fig., Young's modulus of the pure SMPU at very strain was very high, which indicated more stiffness than other samples. The addition of the DBA plasticizer resulted in the increment of SMPU softness, which led to a smaller Young's modulus. The value was almost no change for adding 1% of CNC to SMPU gels compared to 0CNC. However, Young's modulus values were slightly increased of 12.69, 15.71, and 21.17 MPa for 3CNC, 5CNC, and 10CNC, respectively. This is because CNC has good crystallinity properties, so adding a tiny amount of CNC may affect polymer stiffness, increasing young's modulus. In addition, the strain at break of 1CNC was slightly increased, but after adding more than 3% of CNC, the strain tends to decline. Since filling amount of CNC supports the SMPU to enlarge before breakage, adding more CNC to SMPU gel sample will lead to fragility. All samples show plastic deformation because they still have a long elongation time and stretching before breaking the same trend with 0CNC. This indicated that the elastic and plastic deformation properties of the material improved. The addition of DBA plasticizer led to smaller Young's modulus, smaller strain lower tensile stress, and larger strain, and the addition of the small

amount of CNC results in almost no change in tensile properties for 1CNC, 3CNC, and 5 CNC but for 10CNC's results may affect to the actuation.

5.3.2 Dynamic mechanical properties

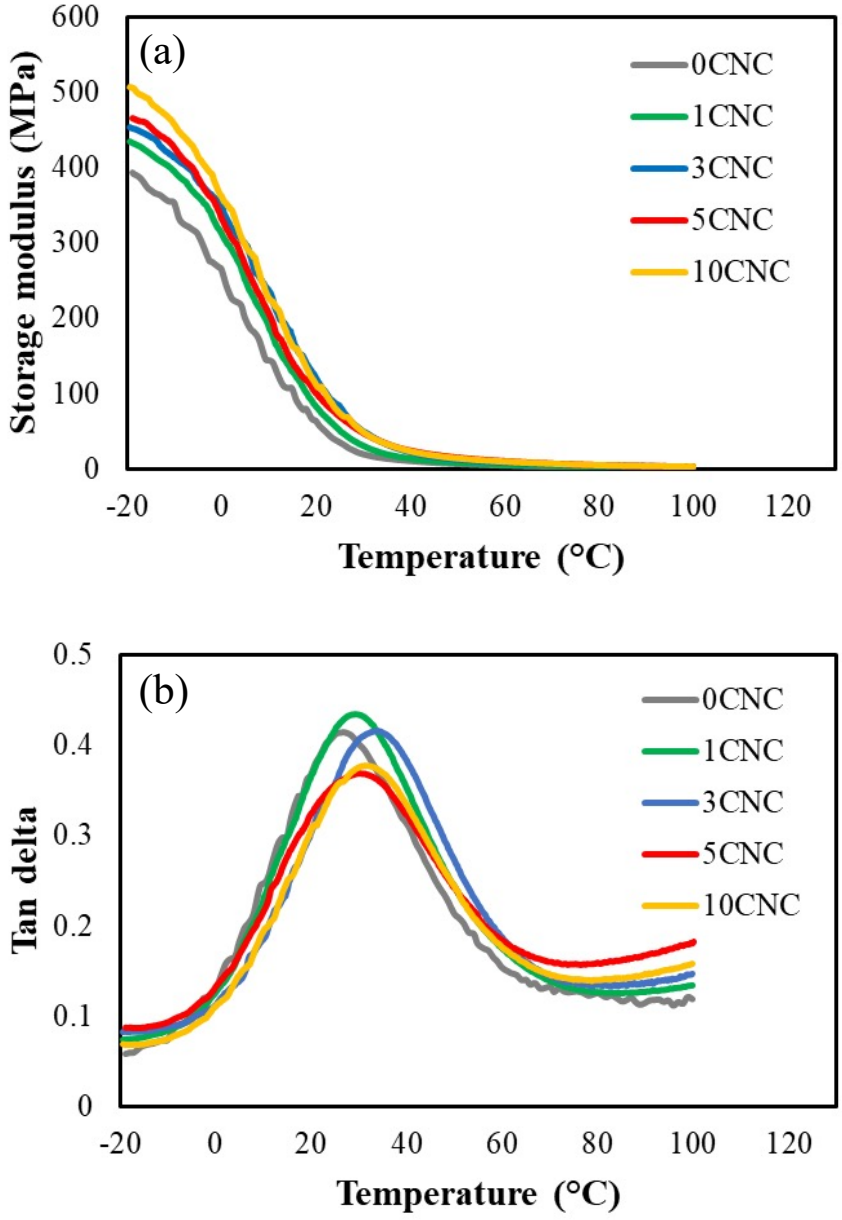

Fig. 5-5 DMA test results of (a) storage modulus and (b) tan delta with increasing temperatures of all SMPU gel samples

The relationship between the storage modulus, loss modulus, and loss factor tan delta will explain the influence of temperature on viscoelastic properties. The good shape memory behavior always necessitated a different status between the lower and upper transition

temperatures. All samples were investigated from −20 °C to 100 °C. At low temperatures, the glassy state modulus refers to elastic energy storage. On the contrary, a rubbery state modulus is observed at high temperatures, which implies entropy elasticity. According to Fig. 5-2a, the storage modulus of 0CNC at low temperatures is extremely high, measuring 3900 MPa. Because the materials are elastic, the storage modulus at high temperatures decreased by two orders of magnitude at high temperatures, demonstrating the shape memory function. At 10% CNC content, the storage modulus slightly increased. However, it significantly increased to 5300 MPa at 10% CNC plasticizer content. The storage modulus increased with increasing CNC content because the hard segment increased in the SMP matrix.

The tan delta is the parameter ratio of the loss modulus to the storage modulus and is represented in damping properties. They demonstrate the difference between two phases in polymer composites. At the low-temperature range, the damping factor is extremely low because the polymer chains are frozen and good for shape fixity. The highest peak between the two phases was referred to the glass transition temperature (Tg) (Fig. 5-2c). The switching in the Tg range was significantly shifted to a higher temperature ranging from 25 °C to 33 °C for adding CNC to SMPU gel and Tg was gradually shifted to 31, 32, and 33 °C for 1CNC, 3CNC, and 5CNC, respectively. Their transition temperatures became closer to human body temperature after increasing the amount of filler. The glassy state was transformed into a rubber state during high temperatures. The developed SMP gels have higher storage modulus and loss modulus, indicating that the elastic modulus of SMP gels increased because of hard segment increment.

5.3.3 Dielectric properties

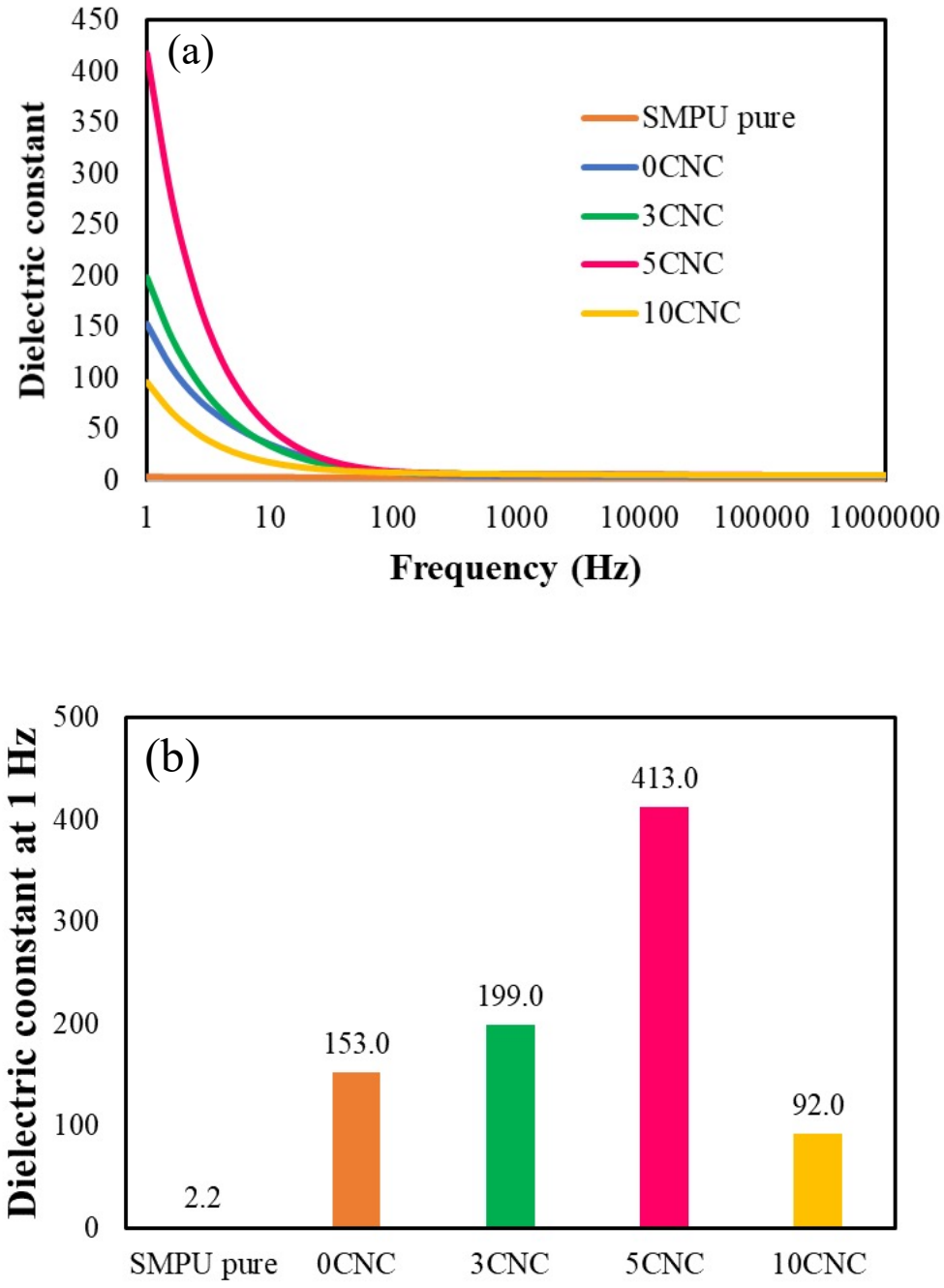

Fig. 5-6a) Dielectric constant of the SMP gels with different CNC contents, b) dielectric constant at 1 Hz

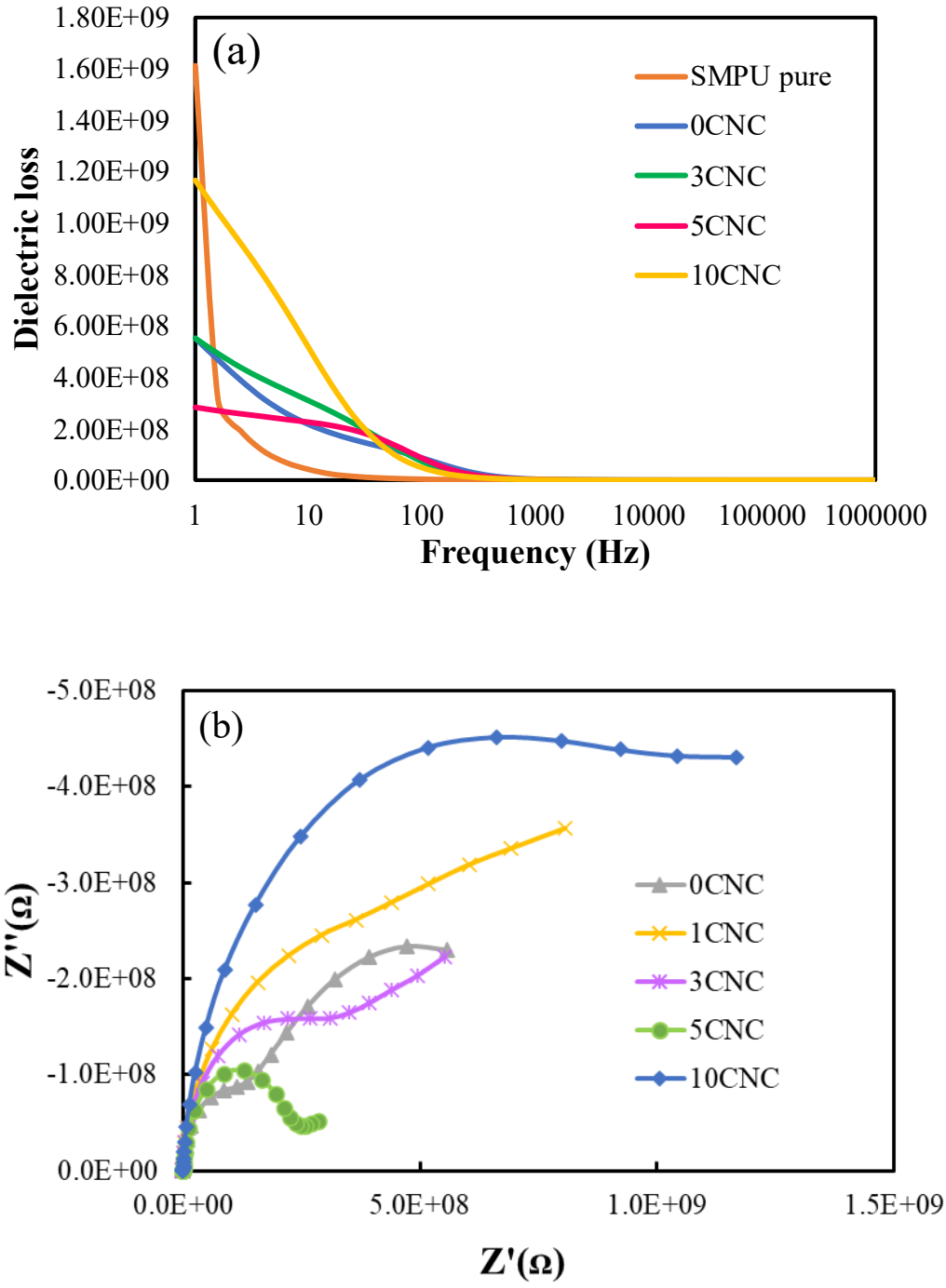

Fig. 5-7 a) complex impedance with real and imaginary components and b) imaginary impedance of the SMPU gels with different CNC contents

One important key factor in fabricating soft dielectric actuators is dielectric properties, which could be investigated by impedance analysis. They will observe the behavior of electric

charging inside SMPU composites and their response to electric stimuli. The interaction of SMPU gel with the electric field led to cause energy storage and energy loss, which is referred to as dielectric constant (ε) and dielectric loss (ε'). Figure 5-5a displays the results of the impedance analysis of the pure SMPU and the SMPU gels with different CNC contents. For all samples except SMPU pure, the dielectric constant is high at 1 Hz and gradually reduced to a constant value as the frequency increased to 10 Hz and became constant above 1000 Hz. The dielectric constant of the SMP gels had a significant frequency dependence in the low-frequency regime. From Fig 5-6b, the dielectric constant of 0CNC was 153, and it was constant for all the investigated samples because of their insulator property. However, adding 10% of CNC to composites affected the dielectric constant at low frequencies sharply increased to 199, which was about 32 times increase compared with the pure SMP. Figure 5-7a shows the results of the impedance analysis. We found that the 5CNC sample had the lowest impedance value, and SMPU pure had the largest impedance value, which indicated that 5CNC has less insulator properties. The dielectric constant of 10CNC became lower than 5CNC, but it was still good sufficient to drive actuation on the intensity of electric field.

To investigate the ability of electric charge transporting by electric field, samples' resistance and conduction could be explained by the imaginary impedance (Z'') and real impedance (Z') curve. From, Fig.5-7b, the results show in semicircle line, which its diameter referred to the resistance of SMPU gels. The 10CNC have a very large semicircle line, so their behavior conducted the lowest electric transfer. However, 5CNC shows the smallest diameter of a semicircle, which mean that they are good at electric charging to carry electron between the electrode and SMPU gel sample, resulting in electrode polarization.

These results demonstrate their potential on electromechanical to perform electric actuation. CNC ‘s structures have hydrogen bonds, which is expected to have a strong point of depolarization. For 10CNC, their behavior can be attributed to the limited interaction between the polymer and filler because of the excessive CNC. Therefore, the dielectric properties of the SMP gels were closely related to the plasticizer properties. Furthermore, impedance control can still support velocity control in human movement motion at a low-frequency range.

5.3.4 Electric actuation

5.3.4.1 Electric response

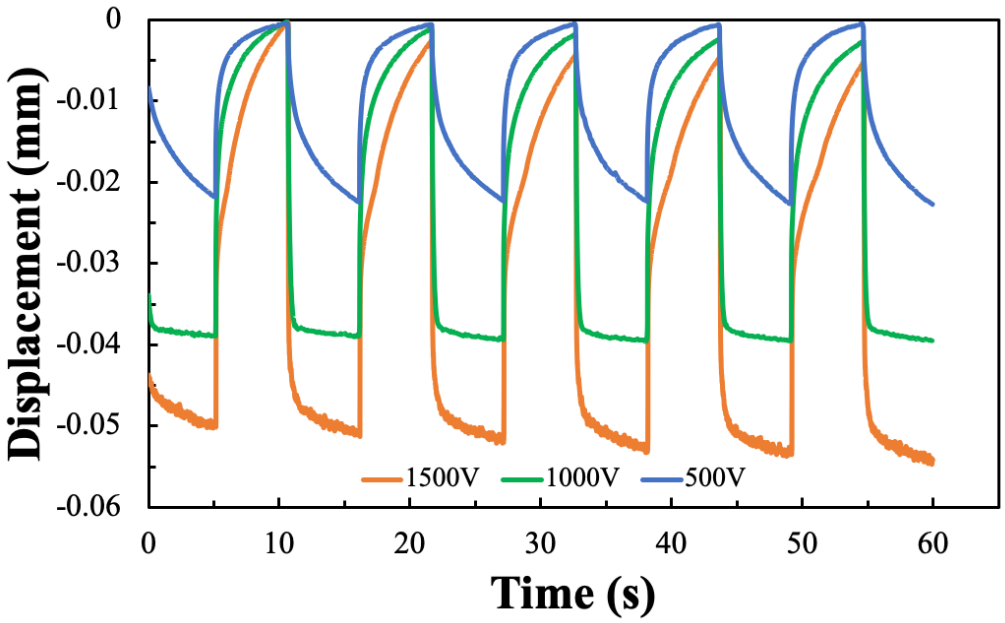

Fig. 5-8 5CNC gel actuator between two conductive electrodes of mesh and foil at 0.1 Hz

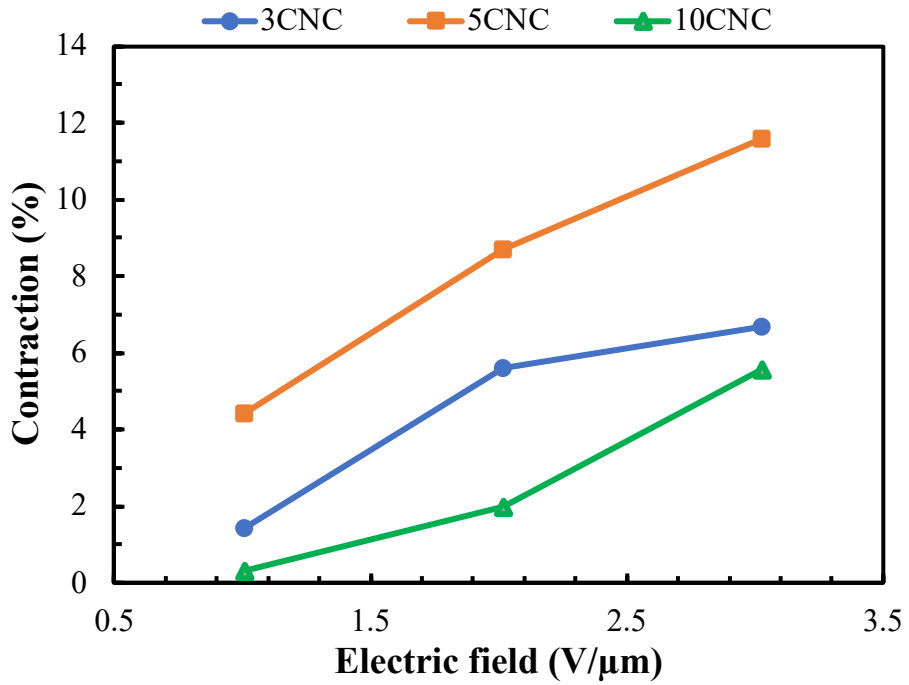

Fig. 5-9% contraction of 5CNC gel actuator

The SMPU/DBA/CNC composite gel actuator consists of the conductive material sandwiched between two conductive electrodes. The electromechanical performance was

investigated in the applied voltage range of 500–1500 V, as shown in Fig. 5-8. We decided to use the electric source at low frequency, which is the same trend with gel sheet actuation. The contraction and expansion of its tube actuator could be attributed to compress deformation on its diameter. The deformation of the gel occurred toward the anode side, and the gel entered the mesh holes. The negative dipole of the DBA and CNC molecule caused it to move to the anode, which resulted in shrinkage, and the resulting deformation was expressed as a reduction of the thickness. On switching off the applied voltage, the gel rapidly returned to its original shape. Figure 8 shows the contraction in the diameter direction. The contraction was 0.027 mm at 1500 V. The largest gap in the deformation occurred when the applied voltage was between 500 to 1000 V, which was increased by about 0.02 mm. This CNC gel actuator showed reversibility under repeated on-off cycling with a switching time of 10 s.

Moreover, contraction occurred rapidly, and this displacement could be maintained. The actuation performance was tested over several cycles and showed stable repeatability. The observed two-way shape deformation can be explained theoretically via electrostriction and Maxwell stress principles. Two types of force are primarily responsible for the deformation: the contraction force caused by switching the electric field on, followed by the Maxwell stress. The results indicate that the 5CNC had good shape recovery under an applied electric field with good reproducibility.

The different kinds of samples were investigated in the electric actuation experiment, and they were compared in the same stage, using the electric intensity and the low range frequency of the electric device. The %contraction strain compared with their thickness is shown in Fig. 5-9. When the 3CNC was actuated by electric field at 10.10 V/um, only slightly on contraction occurred, and the displacement was increased to 5.60% and 6.67% of contraction as the electric field increased to 2.020 and 3.03 V/um, respectively. For the 5CNC gel, there was tiny contraction at a low electric field of 10.10 V/μm, but the increasing contraction was up 11.58% as the electric intensity increased. However, 10CNC gels have smaller contraction compared to 3CNC and 5CNC gels. Since the addition of CNC to SMPU gels was limited to the principle of Maxwell stress because its modulus was significantly increased (in section 5.3.1), and the dielectric constant also decreased compared to other samples (section 5.3.3). The contractions of CNC gels were remarkably increased by increasing the electric intensity, and its values increased from 4.42-11.58%., which obtained the highest contraction strain compared to other samples.

5.3.4.2 Tube deformation

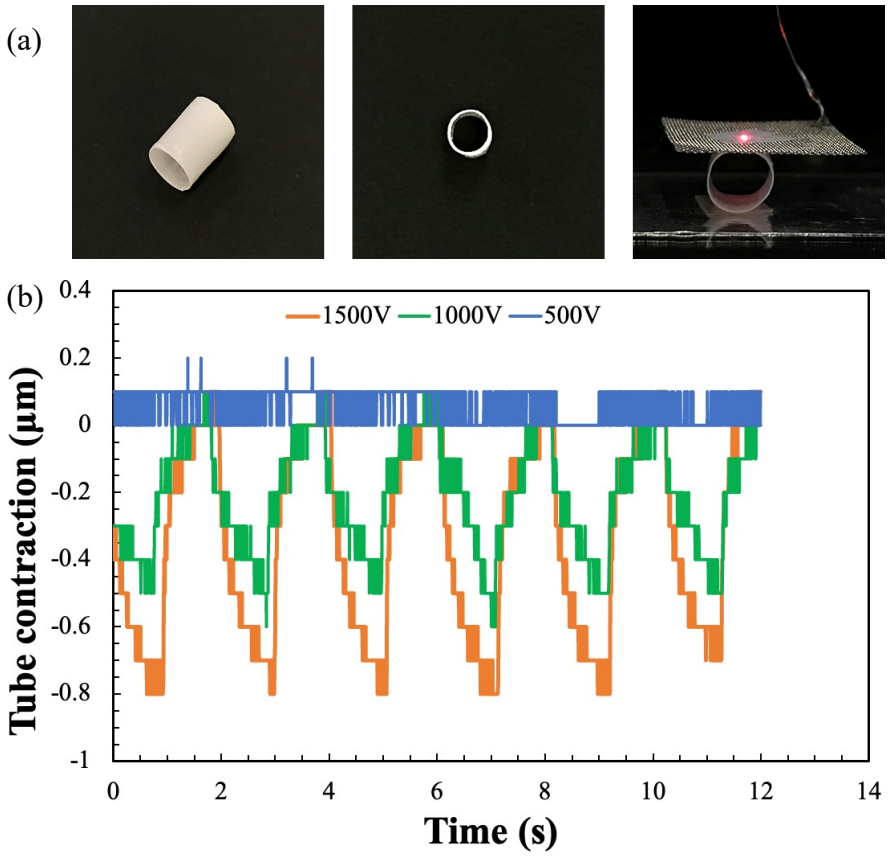

Fig. 5-10 (a) SMPU/DBA/CNC tube on electric actuation and (b) tube deformation under different applied voltages at a frequency of 0.5 Hz

The SMPU/DBA/CNC tube was fabricated by the hot-pressing method in Fig 5.2.3, and their actuator was incorporated with the active material sandwiched between two metal electrodes as Fig.5-10a. The electric source was applied to its diameter direction, and see the results in Fig. There is no deformation occurring at 500 mV however, the tube deformation changes at 1000 mV of 500 um. The most significant contraction on its diameter was 800 µm at 1500 mV, as shown in Fig 5-10b. Compared to its diameter, it was contracted at about 0.02 %. It was much difficult than the contraction on its thickness. The contraction increases with increasing the applied voltage. The results present the same trend with electric actuation on thickness direction. We believe that this tube actuator with tiny displacement is suitable for human implants activated by micro-scale actuation.

5.3.5 Chemical structures

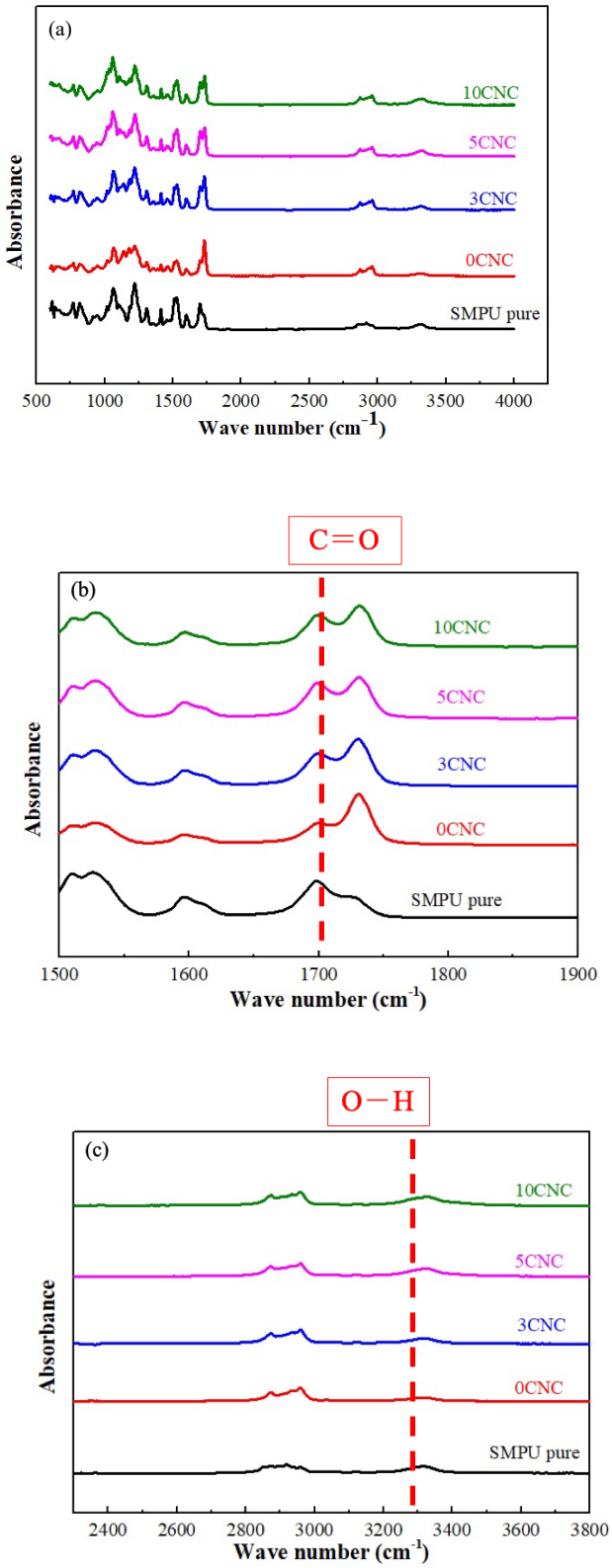

Fig. 5-11 FTIR spectra of the SMPU/DBA/CNC composites of a) 500-4000 cm^{-1}, b) 1500-200 cm-1 and c) 2300-3800 cm^{-1}

The chemical structures of SMPU/DBA/CNC composites were optimized to confirm the material's behavior and the effect of adding CNC on electromechanical performance, shown in Fig 5-11a. The pure SMPU displays the intensity peak at 1700 cm^{-1}, which refers to the C＝O vibration stretching of the urethane group. After adding the DBA plasticizer, the absorption peak of C＝O was shifted to 1730 cm^{-1}, which shows the carbonyl group of DBA plasticizers (see in Fig.5-11b). Furthermore, the intensity peak at 3330 cm^{-1} was obviously appeared after adding the amount of CNC, as shown in Fig.5-11c. The dielectric properties of the SMPU actuator could be improved by adding CNC to its matrix, which contributed to containing the amount of O-H group. However, their dielectric properties tend to be declined since the rich amount of CNC contributed to the increase of the crystalline phase and resulted in the increment of actuator stiffness. The tensile properties and DMA in section 5.3.1 and 5.3.2 also presented the young's modulus and storage modulus increased when the amount of CNC was increased, which confirms that its softness decreased. This characterization of the SMPU/DBA/CNC composites resulted in an enhanced SMPU that was a soft dielectric actuator, and the obtained SMPU gels demonstrated electric actuation.

Furthermore, the 0CNC sample had the largest shifted C=O absorption peak at 1730 cm^{-1}. This explained that 5CNC has the highest dielectric constant value among all samples and acts the most sensitive electric actuation performance. Finally, DBA has been demonstrated as an excellent plasticizer for fabrication gel actuator and CNC filler support not only C＝O group but also enhance dielectric properties due to the negative polarity of its hydrogen groups (O－H).

5.4 Conclusions

In this work, SMPU dielectric elastomer has been fabricated, and their electric actuation performance is investigated for tube designed-actuator applications. The two-way deformation of contraction and expansion was successfully demonstrated, and several soft actuators were fabricated for practical use. The results indicated that the 5CNC had the best contraction and their maximum displacement of 11.58% and the tube was contracted up to 800 mm at 1500 mV. In addition to the electric actuation, the dynamic mechanical analysis showed their viscoelastic properties, and glass transition temperature also improved to be closer to the human body temperature range. The developed SMPU gels were still very flexible. Even CNC was added and could be elongated to a high strain of 523%. The adding of CNC enhanced the dielectric constant. The dielectric constant in SMPU gels was clearly improved at 1 Hz, which allows the developed SMPU gels to function as sensors and actuators under applied electric fields with frequency dependence. Modification by the DBA plasticizers and CNC filler was hypothesized to occur electric polarization in the SMP matrix and improve dielectric properties. The SMP gel was presented to electric actuation on two-way shape memory deformation. Moreover, the CNC phase has the rich O－Hand CO group, which affects the characterizations of SMPU tube actuators under electric fields based on Maxwell stress and presents micro-displacement of two-way shape memory effect during the electric field application. The fabrication of SMPU tubes may provide potential uses such as tube microactuators, biomedical devices, and health care.

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Chapter 6

Biomedical applications of developed SMPU

Chapter 6 Biomedical applications of developed SMPU

6.1. Introduction

Shape memory alloy was used as a human implant device in the past. However, they have several drawbacks, which are too high stiffness and have several side effects inside the human body during long-term use [1-2]. Their fabrication uses high cost to process. Shape memory polymer (SMP) is preferable to fabricate medical devices since they are lightweight, high softness, and easy to process. Recently, the development of shape memory polymer (SMP) has been interesting for biomedical applications. Especially, shape memory polyurethane generally has excellent performance on thermal actuation. Since the Tg of polyurethan-based materials can be activated -30 to 65 °C, which can be tailored by self-shape memory effect for various biomedical uses [3-4]. Mitsubishi Heavy Industries, Ltd fabricated the first commercial SMP and their SMP-based polyurethane in the DiAPLEX series has a good performance on biocompatibility and low toxicity [5-7]. SMPU also has interesting features of composition and other stimuli methods for clinic applications such as ultrasonic, light, and magnetic fields to broaden their applications. For example, the laser-activated shape memory polymer was conducted to remove blood clots [8]. The concept of SMP wire was developed to use as orthodontic braces, and their thermomechanical analysis shows stability over three months.

The SMP micro-actuator has a potential function by using human body temperature-triggering, which can reduce the damage [9-10], and implants for tissue engineering are of enormous interest in medicine. The biodegradable implant materials are attractive for applications like self-tightening sutures inside the human body. In one study [11], thermoplastics with high elastic shape memory were extruded into monofilaments. The suture was programmed by exerting appropriate stress on the extruded fiber and thermal quenching. The suture was loose in the ambient environment. However, when the suture was inserted inside the human body, and the temperature was increased to 41 °C, the shape memory response occurred. As a result, the suture tightened, causing the tissue to contact [12]. Moreover, researchers used the advantage of the shape memory of polymer blends fabricated from thermoplastic PU and polylactic acid to develop catheters [13]. First, the catheter was inserted inside the human body as an organ tube. The catheter became larger and softer when inside the human body because of the shape memory effect. Shape memory nanocomposites were produced by fabricating a bilayer structure of SMPU and silver nanowires [14].

Currently, we have developed these gels for tube applications and investigated their thermal actuation ability to expand the field of thermally induced applications, which has never been studied before. The gels have softness close to human skin, which can be wrapped with human skin- bandage as shown in Fig.6-1a. Tube actuators could be considered as drug delivery tubes (Fig. 6-1b) by controlling the expansion on its diameter in some vital treatment cases or as artificial blood vessels, which could be very tiny when inserted into the small implant and self-expand due to the shape memory effect activated at body temperature (Fig. 6-1c).

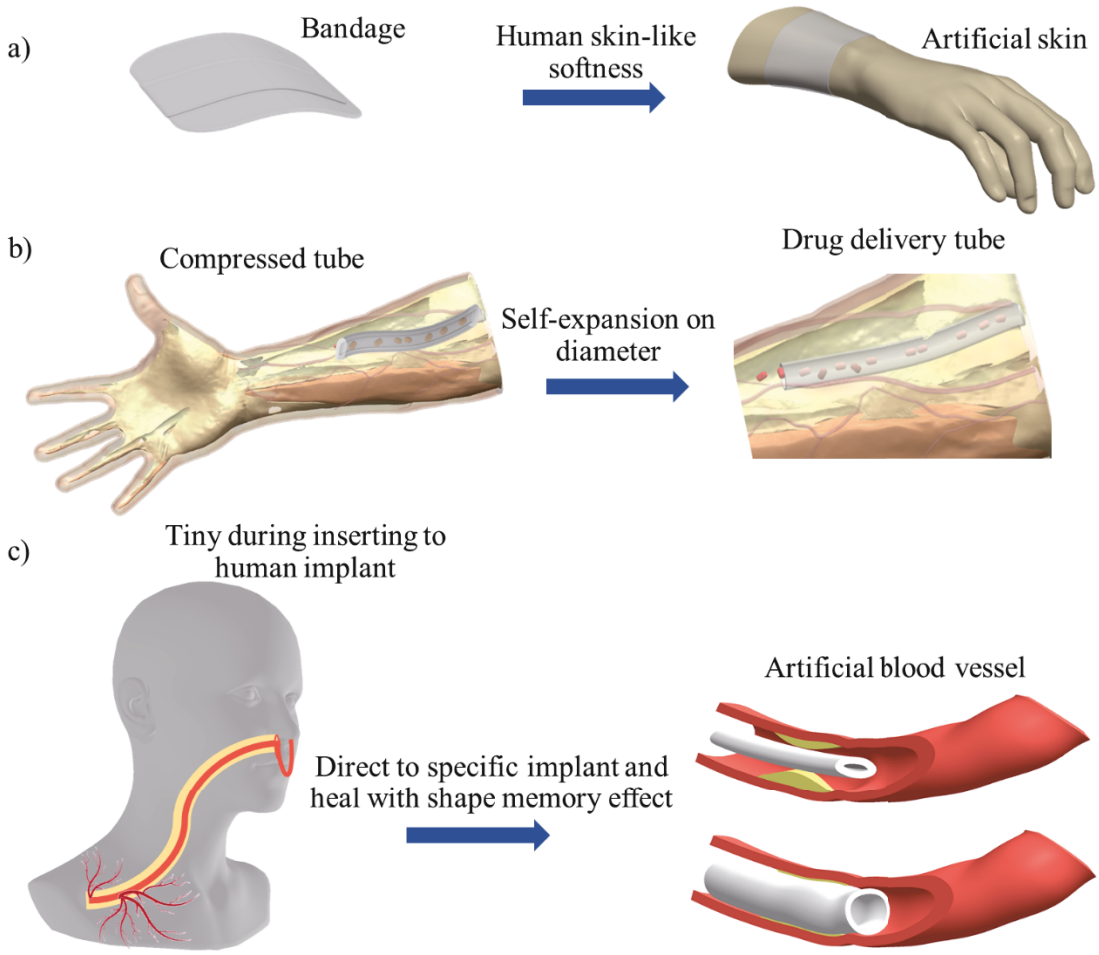

Fig. 6-1 Expected applications of gel tube actuators for (a) drug delivery and (b) artificial blood vessels

This chapter will demonstrate the combining composites to develop SMPU gels and tubes while focusing on toxicity and biocompatibility. The biocompatibility in vitro experiment may demonstrate a new self-healing feature of soft actuators and could be developed as a drug release system by controlling heating levels related to the human body temperature and motion.

6.2. Experimental

6.2.1 Preparation of SMPU gels

Three kinds of samples (pure SMPU, SMPU/DBA, and SMPU/PEG) were used to investigate the biocompatibility. All sample was cut into a round shape with a diameter of 10mm and three replicates per one kind of sample. The sterilization of SMPU gels was performed by deeply soaking the samples in 70% aqueous ethanol solution in a multi-well TCPS dish. After one h, the SMPU gels were washed by using phosphate-buffered saline (PBS) 3 times. The samples were fixed by using glass tubes placed on them to prevent the sample from floating in the medium solution.

6.2.2 Cell culture and preparation

NIH 3T3 cells (derived from mouse embryonic fibroblasts) were used in this experiment. As one of the most utilized cell lines, their cell line has been used in a range of mechanistic and cell-based assays, including protein functional analysis. Moreover, they are easy to grow and process [15].

The cells were washed with (PBS). Enzyme trypsin was added to the cells to ensure that they were movable. Eagle's minimal essential medium was used as a control. The cells were seeded into 96-well plates with a density of 1×10^4 cells/well by taking 5mL of Eagle's MEM in a centrifuge tube and adding the cells carefully from the microtube. The microtube was washed to take all cells and centrifuge at 900 rpm for 5 minutes. The solution was taken 10mL and put in a beaker. After that, 5mL of the Eagle's MEM was added to a dish and add 5mL of the solution. Finally, all cells were checked their living by light microscope and kept in an incubator at 37 °C in air containing 5% CO_2 (shown in Fig.6-2).

Fig. 6-2 Photographs of the cell culture experiment

6.2.3 Scanning electron microscope (SEM)

The samples were cultured with NIH3T3 for 8 h and washed twice with a PBS solution to remove unattached cells. To fix the attached cell on the samples ' surfaces, the glutaric dialdehyde solution (2.5%) was added to the wells. The samples were stored in a refrigerator for 24 h. Further, the samples were rewashed with the PBS solution. To dehydrate the solution, varying ethanol concentrations of 50%, 70%, 90%, 95%, and 99.5% were added to the samples for 30 min per concentration. Then, the samples were freeze-dried at −80 °C for 24 h to prevent cell shape shrinkage. Platinum was used to coat the samples' surfaces. Finally, scanning electron microscopy (SEM) was used to capture images and evaluate cell behavior on the surface.

6.2.4 Cell adhesion

NIH3T3 concentration cell suspension aqueous solution with Minimum Essential Medium (MEM) was prepared to use for the cell adhesion test. The cells were poured on the sample well. The cells adhesion on SMPU gels were evaluated after 24 hours by calculating the number of cells attached to each sample.

The cell adhesion was conducted to investigate the number of living cells on the samples' surface. Moreover, cell proliferation was performed to optimize cell growth after 1, 3, and 7 days and the results were investigated by lactate dehydrogenase assay.

6.2.5 Cell proliferation

The cell proliferation was performed to optimize the cell growth after 1, 3, and 7 days and the results were investigated by lactate dehydrogenase assay (LDH). The calibration solution was prepared by a solution of 50,000 cells/ml. The calibration solution was poured in 5 microtubes with volume differences as follows: 100 ml, 200 ml, 300 ml, 400 ml, and 500 ml. Then, the PBS solution was added to 1000 ml in total to get a concentration of cells of 5000 cells, 10,000 cells, 15,000 cells, 20,000 cells, and 25,000 cells, respectively. The calibration curve was obtained by measuring the absorbance value from five calibration solutions to calculate the number of cells. After that, the samples were taken out from a medium solution in the incubation and dipped to rinse with PBS. For determination of the adhered cells by LDH assay, the cell solution was poured into wells of a 96-well plate, and each sample was tested with LDH assay.

The LDH activity was immediately measured by ultraviolet absorption at wavelength 340 nm using a Thermo Scientific Multiskan FC microplate photometer (Thermo Fisher Scientific Inc.). The enzyme activity of LDH can observe from the chemical reaction of LDH when it is released into the cell's medium from the damaged or dead cells because of cell membrane damage. LDH converts lactate using NAD as a coenzyme and performs pyruvic acid and NADH. The number of living cells was calculated from the calibration curve obtained by the relation between the number of cells and absorbance value at 340 nm of NADH [16-17].

6.3 Results and discussion

6.3.1 Morphology

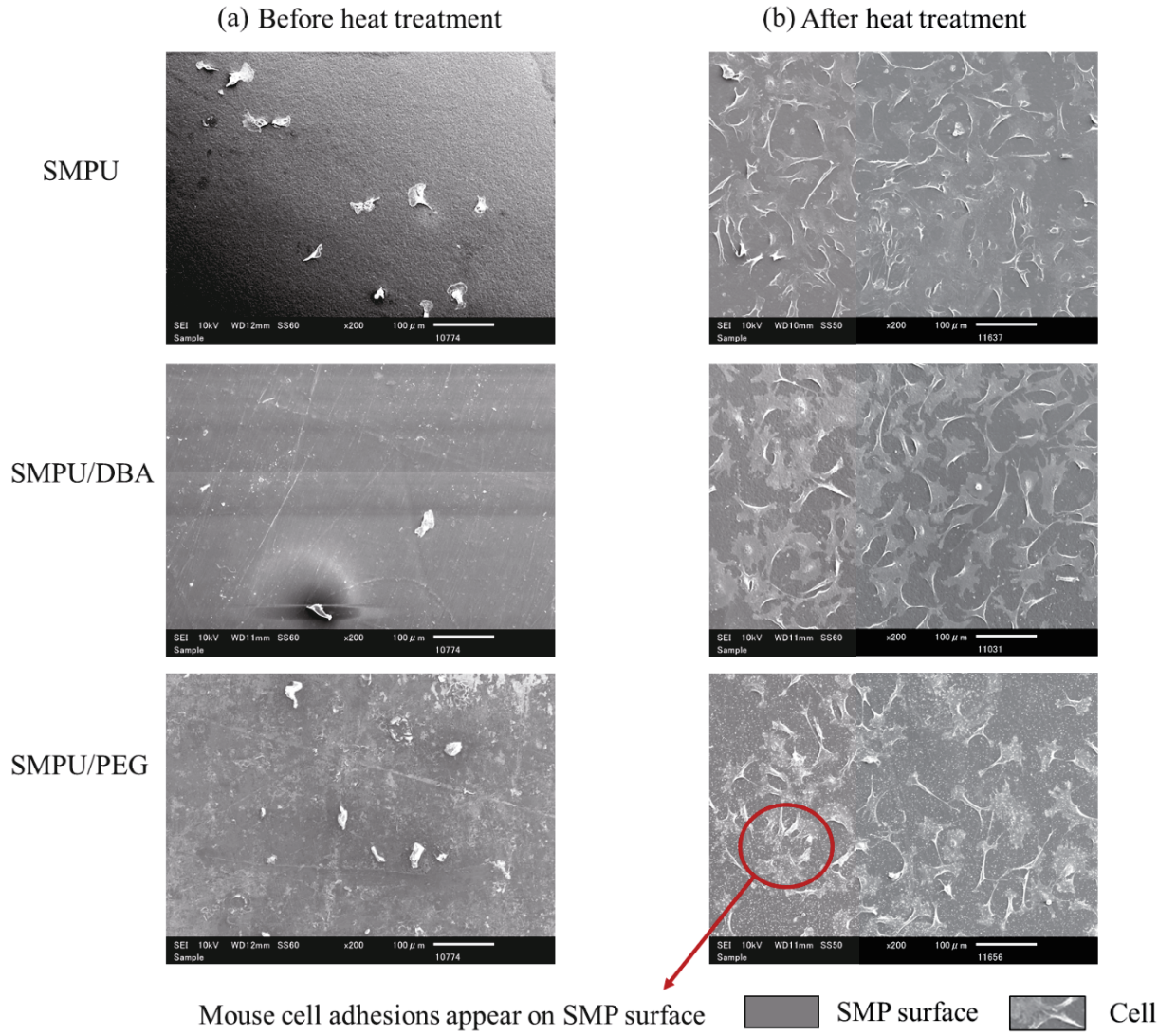

Fig. 6-3 Morphology of NH3T3 cell adhesion on SMPU gels (a) before heat treatment and (b) after heat treatment

Fig. 6-3 shows the morphology of NHI3T3 cells on contained cells adhered to the sample surface. Without treatment, the cell shape is not flat, and could not find many cells appear on their surface, as shown in Fig. 6-3a. However, after heat treatment, many cells adhered to both samples, and cells on surfaces were flat shaped and adhered to neighboring cells (Fig. 6-3b). Since the solvent was removed and cleaned their surface clearly, this is an indication of cell activation. All samples show little variation in cell appearance on the

surface, implying that DBA and PEG plasticizers do not interrupt cell attaching behaviors compared with pure SMPU.

6.3.2 Cell adhesion

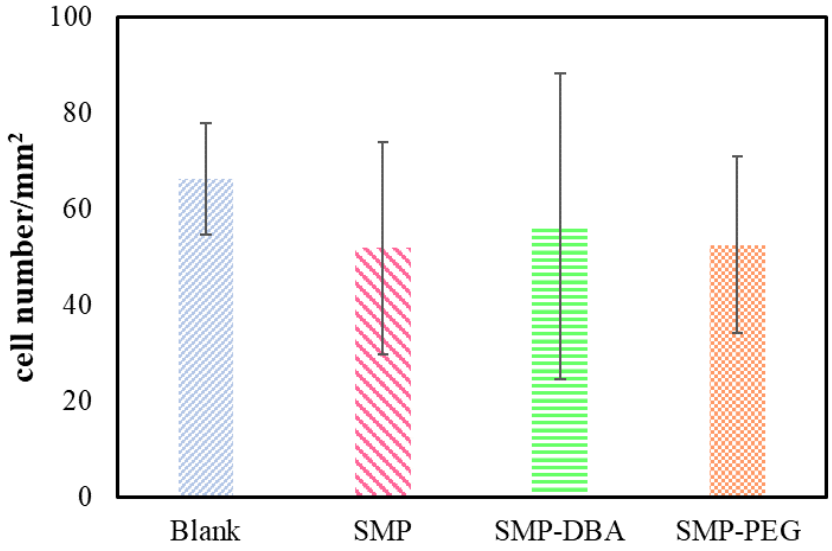

Fig. 6-4 NH3T3 cell number results on SMPU, SMPU/DBA, and SMPU/PEG gels adhesion on their surface

Cell adhesion is an important factor in demonstrating the relationship between materials and living cells. Many studies have reported that SMPU is biocompatible with living cells and can be used in biomedical devices, but the combination of SMPU/DBA plasticizer and SMP/PEG has never been reported. These SMPU composite gels could be used to create materials for tissue engineering. The results of the cell culture test for 24 h and the number of living cells in all samples was close to that of the tissue culture polystyrene (TCPS) blank control. Further, the number of cells on their surface for all samples is not significantly different. (Fig. 6-4).

6.3.3 Cell proliferation

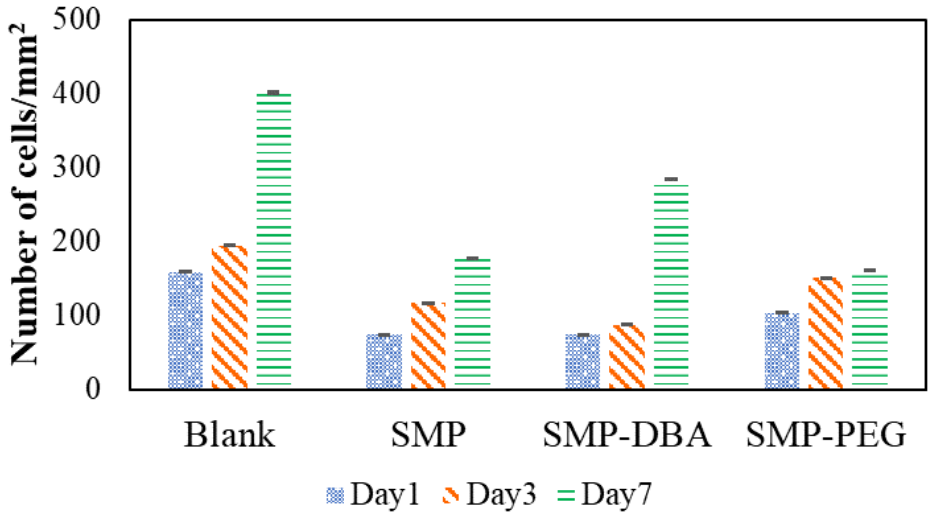

Fig. 6-5 NH3T3 cell number results on SMPU, SMPU/DBA, and SMPU/PEG of cell proliferation after 1, 3, and 7 days on the gel surface

The cell proliferation was conducted for 1, 3, and 7 days to investigate more biocompatibility possibilities, as the NTH3T3 mouse and human fibroblasts have a similar trend of cell growth behavior. Fig. 6-5 shows that the living cells of SMP and SMP-10 slightly increased after 3 days, compared with 1 day, and they significantly increased after 7 days. This indicated that SMP and DBA composites could promote cell proliferation, with SMP/DBA having a slightly higher cell growth number than SMPU. This is due to the material's increased flexibility and swollen networks, making it easier for the cells to adhere to the surface. On the other hand, SMP/PEG has less cell growth than SMP and SMP/DBA. It shows that SMP/DBA has better biocompatibility performance, but SMPU/PEG also does not hinder cell growth. This experiment indicates that cells have the ability to attach and grow on the material and further confirms in vitro biocompatibility of SMPU gel composites.

6.4 Conclusion

SMPU generally shows good performance on biocompatibility, and they are common use in the biomedical field. Researchers have reported that the DBA test on animal cells and some of these studies have been used in cosmetics development. This study combined these two components and reported the test results of SMPU and DBA plasticizers in vitro experiments to expand the possibility of fabricating bioactuators in the future. Based on these experiments, SMPU doped with DBA plasticizers exhibit good biocompatibility, and SMPU doped PEG has non-toxicity. This investigation confirmed that SMPU gels composite-based tube actuators can be used on or inside the human body.

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Chapter 7
General conclusion

Chapter 7 General conclusion

In this work, SMPU gel actuators have been fabricated as dielectric elastomers, and their shape memory property and actuation performance are investigated for soft actuator applications. The two-way deformation of contraction and expansion was successfully demonstrated, and several soft actuators were fabricated for practical use. The main results indicated as follow:

In the chapter 2, the fabrication of an SMPU gel incorporating plasticizers has resulted in the softness and dielectric properties, which are two main factors to develop SMPU gels for electric actuation. (1) The young's modulus was significantly decreased with the increasing amount of DBA up to 15 times (SMP-4DBA) compared to SMPU pure. It indicated that DBA successfully improves the softness of SMPU composites and is easy to deform at a lower temperature. (2) DBA could change the SMPU properties from insulator to dielectric. The dielectric constant of gel was improved, and SMP-2DBA has the most excellent dielectric constant value at 153. The use of DBA plasticizer enhanced the softness of gels and markedly increased the dielectric constant. The dielectric constant in SMPU gels was clearly improved at 1 Hz, which allows the developed SMPU gels to function as sensors and actuators under applied electric fields with frequency dependence.

In the chapter 3, the SMPU gel actuators were shown to have both electric and thermal actuation. The temperature activation contributes to quick recovery and exhibits a one-way shape memory effect. Moreover, the characterizations of SMPU gel actuators under electric fields are based on the principle of Maxwell stress, which shows a two-way shape memory effect of contraction and expansion when the electric field is ON/OFF. The shape recoverability was studied by thermally induced. SMPU incorporating with DBA is a much higher strain compared with SMPU pure. The shape memory effect of SMP-1DBA and SMP-2DBA could be rapidly recovered after removing stress, much faster than was the case for neat SMP. The shape recovery ratio is up than 99% and trend to increase with the number of cycles. The SMPU gels were observed by an electric field. SMP-2DBA has a maximum displacement of 0.20 mm at 3.42 V/um. It was increased about 200% compared with a driven electric field at 10.27 V/um. When the electricity was discharged, they could recover immediately to their original shape.

In the chapter 4, The developed SMPU gel tube for thermal actuation was improved by adjusting the concentration of plasticizers and designing methods for tube actuators. The softness was adjusted close to the softness of human implants, and temperature stimuli

contributed to a great elongation of up to 900% by plastic deformation. Remarkably, the glass transition temperature was controlled and significantly lowered from 60 °C to 37 °C, close to the human body temperature range. The tube compression and expansion demonstrated tube recovery in the diameter direction up to 83% for SMP-10 gel, and their significant recovery behavior started from 37 °C. This behavior shows that DBA plasticizer incorporated SMPU has a faster shape recovery rate at lower temperatures than pure SMPU. Furthermore, DBA - incorporated SMPU have maximum recovery stress of 2.06 MPa, which shows that they are safe for use in the human body.

In the chapter 5, The SMPU tube for electric actuation was improved by adding CNC to SMPU gel composites. Adding 5%w/v of CNC to SMPU gel composites could enhance the dielectric properties since their dielectric constant was improved up to 413, which is 2.7 times increase, compared to adding only DBA plasticizer. Moreover, their glass transition temperature was enhanced close human body temperature range. Its actuator contraction was occurred up to 11.58 % on the thickness direction, and the tube actuator deformation was contracted up to 800 μm in the diameter direction.

In the chapter 6, these SMPU gel actuators are expected to use for biomedical applications. The biocompatibility in vitro experiment was conducted to investigate their non-toxicity. Therefore, the cell culture of four kinds of SMPU gel samples (SMPU, SUMP-DBA, SMPU-PEG) was culture to investigate cell adhesion, cell proliferation, and morphology. All samples do not have toxicity. The shape and variation of cells exhibit living signs. Additionally, cell proliferation of SMPU and SMPU-DBA have better biocompatibility than SMPU-PEG due to the number of living cells.

The use of shape memory polymers in dielectric actuators with low frequency is safer and more suitable to the human body. The fabrication of SMPU gel and its scale-up or down is not difficult, and its flexibility is also controllable, which may endow potential uses such as medical assistance devices, bandages, and artificial muscle. In addition, the cell adhesions and proliferation of NH3T3 mouse cells demonstrate that these SMPU gel and its tube actuators can be used in the human body, which has aided our work on drug release systems for biomedical applications. In the future, SMPU–DBA gels are also expected to be used in producing thermal tube actuators for drug delivery, artificial blood vessels, and other aspects of tissue engineering.

Achievement

List of publications

Journal Publications

1. S. Pringpromsuk, H. Xia, Q.Q Ni, Multifunctional stimuli-responsive shape memory polyurethane gels for soft actuators, Sensor and Actuator A. 313 (2020) 112207.
2. S. Pringpromsuk, H. Xia, Q.Q Ni, Thermal triggering on plasticized shape memory polyurethane actuators and its tubes target to biomedical applications, Sensor and Actuator A. (2021) 113164.

International Conference

1. S. Pringpromsuk, Q.Q. Ni, Development of Shape Memory Polymer (SMP) Films by Plasticizers. The 11th Textile Bioengineering and Informatics Symposium Advanced Materials and Smart Wearables (TBIS 2018), Manchester, UK, July 25–28, 2018.

2. S. Pringpromsuk, Q.Q. Ni, Development of Dielectric Shape Memory Polymer (SMP) Films by Plasticizers. Textile Summit 2018, Nagano, Japan, September 20-22, 2018.

3. S. Pringpromsuk, Q.Q. Ni, Heat triggering of shape memory polyurethane for biomaterials. The 19th International Conference on Biological Inorganic Chemistry (ICBIC 2019), Interlaken, Switzerland, August 11-16, 2019.

4. S. Pringpromsuk, H. Xia, Q.Q. Ni, Development of multifunctional stimuli-responsive shape memory polyurethane for soft actuators target to biomaterials. 2021 China-Japan Academic and Technical Exchange Conference on Composite Materials, China, August 25-28, 2021.

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