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Microstructure Evolution of Liquid Crystal Elastomers by Both Mechanical Deformation and Temperature

기계적 변형과 온도에 의한 액정탄성체의 구조 변화

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Microstructure Evolution of Liquid Crystal Elastomers by Both Mechanical Deformation and Temperature

Advisor: Woong-Ryeol Yu

by

HyeJi Kim

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Department of Materials Science and Engineering Graduated School Seoul National University

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지도 교수 유 웅 열

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> 서울대학교 대학원 재료공학부 김 혜 지

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위 원	년 장	안 철 희	(인)
부위	원장	유 웅 열	(인)
위	원	이 명 규	(인)

Abstract

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Liquid Crystal Elastomers (LCEs) are lightly crosslinked polymers incorporated with rigid and anisotropic liquid crystal molecules (mesogens). The liquid-crystalline ordering of such mesogen in nematic monodomain LCEs brings about reversible shape memory performance by the isotropicnematic transition. Due to the reversible shape memory behavior, LCEs are used in various applications, e.g., smart fibers, 4D printing, soft robotics, biomedical engineering, smart coatings, etc. There are two main parameters that affect the anisotropic ordering of mesogens: temperature and mechanical strain. This research was aimed to investigate degree of orientation of mainchain in LCE under both varying temperature and mechanical strain via in *situ* wide angle X-ray scatterings (WAXS) analysis. LCE was synthesized by two-stage thiol-acrylate Michael addition. Mesogenic acrylate monomers (RM257, excessive acrylate 2 mol%), flexible polymer chain of 1,3propanedithiol, and PETMP crosslinker were used. WAXS analysis was

carried out to observe the anisotropic orientational behavior of mesogens in prepared LCE when various temperature and mechanical force were given. *In situ* WAXS analysis revealed that as the temperature approaches Ti, isotropicnematic phase transition temperature, the change of degree of orientation becomes more influenced by thermal energy than the mechanical strain. Dynamic mechanical analysis (DMA) was also carried out to identify this inflection temperature at various temperatures, finding about 70°C temperature through relaxation test. Finally, the orientational behavior of mesogens in LCE was quantitatively established as a function of temperature and mechanical strain, enabling to simulate the deformation behavior of LCE considering its microstructure.

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1. Introduction

1.1. Background

Liquid Crystal Elastomers (LCEs) have been remarkably brought attention as a soft stimuli-responsive material for their use in actuation. LCEs are soft elastomers with incorporated rigid rod-like liquid crystal molecules, in other words, mesogen molecules [1-4]. This structure gives rise to the orientational order of mesogen molecules being influenced by a stress on the polymer network, and, conversely, orientational order of mesogens decides the shape of the LCEs [5]. Mesogen molecules bring about a unique property of anisotropic thermomechanical behavior by changing their microstructure [6]. The mesogens are randomly oriented at high temperature (isotropic state) due to thermal energy but align in a particular direction owing to steric interactions below a nematic-isotropic temperature (nematic state) [7]. The degree of orientation of LCEs, and consequently the change of shape, is determined by temperature. Reversible shape memory behavior endowed LCE to be applied to functional clothing, shoes, 3D/4D materials, artificial muscles, smart robotics, etc. [8-12] (Figure 1). Therefore, the control of macroscopic mesogen molecules orientation is crucial for obtaining the useful functionalities of LCEs because actuation performance, work capacity, energy dissipation, and elastic modulus of LCEs are all dependent on the alignment of mesogens [12, 13].



Fig 1. (a) Reversible color-morphing and shape-morphing LCE cone. Gained from the reference [14] **(b)** Broad range of LCE application

Two-stage method is one of the most energy efficient and robust way to construct LCEs with desired structures by using click chemistry [13]. The first step is a thiol-acrylate Michael addition reaction which leads to the polydomain LCE networks. In the second step, polydomain LCE is given a physical elongation in a uniaxial direction to induce alignment of mesogens in one direction temporarily, that is, monodomain nematic networks. Subsequently, unreacted acrylates during Michael addition are photo-polymerized under UV light; therefore, they are permanently fixed in a monodomain shape. Despite the uniaxial stretching, anisotropic and inhomogeneous stretch can model various mesogen molecular orientations in LCEs by multiaxial mechanical deformations[15]. This mechanical force- photo crosslinking technique has been widely used to construct thermotropic LCEs facilely and effectively [16]. Therefore, this research is following this method to synthesize LCEs.

The orientation of molecules in LCEs is decided by the temperature and the mechanical deformation (Figure 2). As the temperature increases, the arrangement becomes random while when the strain is given, the molecular orientation is aligned. This implies that the temperature and the external force compete for the orientation of liquid crystal molecules. To the best of our knowledge, however, there needs to be more research on the orientation of LCEs by varying both temperature and mechanical strain and making both factors compete. It has been studied how temperature and mechanical deformation independently affect the orientation of mesogen molecules. Finkelmann investigated the orientation behavior of the nematic main-chain elastomers under strain [17]. He found a critical strain point where the mesogen alignment is no longer oriented. Nematic order parameter was determined as a function of imposed strain at temperature of 35°C and 45°C. Yasuoka explored mesogen movement in main-chain and side-chain LCEs by uniaxial elongation using molecular dynamics simulations [18]. The orientational order parameter of the mesogens along the elongation axis was observed, so they directly noted the microscopic dynamics of LCE molecules. When it comes to the effect of temperature on the orientation of mesogens, they found out that the order retained in LCEs is disrupted by thermal energy. For applications in artificial muscles, Finkelmann in 2001 compared side chain and main chain LCEs over a range of temperature and a range of strain[19]. Order parameter was calculated from the azimuthal intensity distribution at wide angles. They clearly indicate that nematic networks with liquid crystal main chain polymers improve the mechanical actuating ability. Finkelmann, in 2007 investigated the orientation behavior of side chain LCEs by IR-dichroism measurements with temperature dependence [20]. In addition to that, molecular orientation in LCEs was investigated by polarized FTIR and Raman spectroscopies [21]. The transition temperature of LCEs can be modified with constituent parameters. Hence, accounting for the temperature effect on the orientation of mesogen molecules, there exist papers about the orientational order parameter of thermotropic LCEs by varying constituent parameters: mesogen type, mesogen concentration, crosslinker type, and component concentration [5, 6, 22].



Fig 2. Schematic of alignment of LCEs dependent on the strain and temperature

Due to the broad range of applicability, numerical models are required to improve our understanding of the fundamental mechanics regulating LCEs behavior and to enable the predictive modeling of their behavior under different conditions for various applications [23, 24]. Modeling for predicting the thermo-mechanical behavior of complex structures in real-world applications, a strong understanding of the anisotropic mesogen molecules structure is necessary for the effective and specific utilization of LCEs at hand [23, 25, 26]. The optimal approach for the given application requires a deep knowledge of coupling behavior with the elastomer network and changes in microstructure from external stimuli [27, 28].

Therefore, a careful evaluation of the coupling behavior should be generated from externally applied fields. Although a significant amount of theory has been developed to describe the elastic and liquid crystalline behavior of LCEs, limited numerical models exist that can predict the development of monodomain and polydomain liquid crystal structure under severe deformation [29-31].

Their structure–property relationship has yet to be thoroughly investigated. To establish a relationship between microstructure from external effects and anisotropic properties of LCEs, a continuum model needs to be implemented numerically using constitutive equations, which can be set up by quantifying the liquid crystal coupled elastomer deformation. To that end, anisotropic behavior of LCEs by external stimuli should be explored experimentally so that this provides a computational framework that takes into account finite deformation, liquid crystal domain structure evolution, and thermo-mechanical effects.

1.2. Purpose of Research

Understanding the fundamental thermo-mechanical properties of LCEs experimentally is significant, so it becomes possible to establish the congruent governing equation to control the soft elasticity of LCEs as various applications. In this paper, we are aimed to quantitatively establish the orientational behavior of liquid crystal molecules in LCEs as a function of temperature and mechanical deformation by varying both temperature and strain using Dynamic Mechanical Analyzer (DMA) and WAXS.

2. Materials and characterization

2.1. Sample preparation



Fig 3. Chemical structure of monomers to produce main-chain LCE in this study. Mesogen monomer (RM257), Linear chain extender for linking mesogens with dithiol functional end group (PDT) and Crosslinking monomer with tetrathiol functional end group (PETMP) polymerized via Michael addition.



Fig 4. Monomers polymerized by Michael addition, producing polydomain LCEs with unreacted acrylate functional groups. Synthesized polydomain LCEs are stretched in one direction to form a monodomain LCEs. Unreacted excessed acrylates are radically photopolymerized to permanently fix the shape of the LCE films.

Main-chain liquid crystal elastomers were synthesized by a two-stage method. The first stage of the method is the thiol-acrylate Michael addition which led to the formation of network among the monomers. The second stage is the radical photopolymerization to obtain the programmed shape of the LCE samples. During the first stage, diacrylate mesogen (RM 257, 64 wt%) and inhibitor 2,6-di-tert-butyl-4-methylphenol (BHT, 1.5 wt%) were dissolved in toluene (19.2 wt%) at 85°C for 30 mins. Subsequently thiol functional groups monomers, crosslinker (tetrathiol-PETMP,2.7 wt%), chain extender (1,3-PDT, 10.3 wt%), and photo-initiator (Phenylbis(2,4,6-trimethylbenzoyl) PPO, 1.5 wt%) were added to the mixture and reheated to 85°C for 3 mins. The ratio of the acrylate and thiol functional groups was

calculated as 2 mol% in excess of acrylate functional groups than the stoichiometric amount. Shortly catalyst (Triethylamine, 0.77 wt%) was diluted. The solution was degassed under vacuum at 85°C for 2 mins for the fast thiol-acrylate Michael addition reaction. Then the solution was transferred to the glass mold where the two glass slides with 1 mm polytetrafluoroethylene spacers between slides. The mixture was polymerized at room temperature for 2 days, showing transparent elastomer film. Toluene was extracted under vacuum at 85°C until the material reached a stable weight. Elastomers were opaque white at room temperature indicating a liquid crystalline phase in the polydomain conformation.

In the second stage, monodomain LCEs (mesogen oriented to along direction) were formed by uniaxial stretching to the strain. After stretch to 100%, the radical photopolymerization was initiated by exposure to 365 nm wavelength ultraviolet light for up to 90 mins. during which excess acrylate groups reacted to form new bonds in the network. In this way, monodomain mesogen alignment was achieved permanently by radical photopolymerization in the stretched shape, which provide the reversible shape memory properties of LCEs.

2.2. Thermo-mechanical Analysis of LCEs

Dynamic mechanical analysis was carried out to investigate the thermomechanical properties of LCEs with a dynamic mechanical analyzer (DMA Q800, TA Instruments, New Castle, DE, USA). LCE films with 8mm width and 1mm thickness were clamped with 5mm grips. All tests were performed at an oscillating frequency of 1 Hz and preload force 0.01N.

To obtain the storage modulus (E') and loss tangent (tan δ), sample was first heated to 150 °C and stabilized for 10 minutes to reach the thermal equilibrium. Temperature was ramped down to -20°C at a rate of -3°C, allowing uniform heat transfer throughout the sample. It was thermally cycled from isotropic phase to glassy nematic phase. The storage modulus and loss tangent graph as a function a temperature were obtained from the test. The glass transition temperature (Tg) and nematic-isotropic transition temperature (Ti) of the LCE samples were determined as the temperature where the peak of tan δ curve and the temperature where the minimum of the E' curve respectively.

Stress relaxation experiment was also performed through DMA to identify the inflection temperature point where the change of degree e of orientation of mesogens in LCEs gets more influenced by thermal energy than the mechanical strain. The sample was stretched 100.00%/min to 100.00% and maintained for 30 minutes in an isothermal condition.

2.3. Wide Angle X-Ray Scattering

Wide-angle X-ray scattering (WAXS) measurements were performed using a Xeuss2.0 instrument to quantify the degree of orientation of mesogens in LCEs at various temperature. The instrument was equipped with a reversed-biased silicon diode array sensor. The wavelength of radiation (λ) was 1.54189 Å and the sample to detector distance was 70mm. The scattering patterns were collected with 487 x 619 pixels (pixel size: $172 \times 172 \mu m^2$).

WAXS samples were prepared as following figure 5 before the characterization since it was not a strain *in situ* equipment. The LCE sample was stretched 100% in the heating chamber, which was set to the desired temperature. Then the extended sample was immediately secured to the slide glass with black tape to prevent it from returning to its original shape. For the sample prepared this way, the part between the black tape was cut and characterized by WAXS.



Fig 5. WAXS sample preparation

2.3.1. In situ X-ray measurements

For the supporting data, *in* situ WAXS analysis was carried out. For the *in situ* WAXS measurements, beamline 9A U-SAXS at Pohang Accelerator Laboratory (PAL) in Korea was used. The X-ray wavelength was 0.1118 nm. For tensile tests, the prepared samples were gripped into a home-built tensile machine equipped with an electronic controller and capable of uniform stretching. The initial distance between the two grips was 30 mm and the stretching rate was set at 100%/sec for all *in situ* experiments. The typical image acquisition time for the WAXS experiments was 3 sec, including 2 sec for detector readout time.



Fig 6. In situ WAXS (a) Sample peripherals (b) tensile equipment

3. Results and discussion

3.1 LCE transition temperatures and dynamic mechanical properties

Dynamic mechanical analysis (DMA) was conducted to understand the thermomechanical behavior of LCEs as a function of temperature.



Fig 7. (a) Storage modulus curve of LCEs resulting from the DMA test. Testing was performed using a temperature ramp rate of 3° C/min at an oscillating frequency 1Hz. Nematic-isotropic phase transition temperature is defined ~ 90-100^{\circ}C. (b) Tan delta curve of LCEs resulting from the DMA test. Testing condition is the same as (a). Glass transition temperature was observed ~ 20 °C.

Storage modulus (E') and loss tangent (tan δ) curve as a function of temperature were obtained to define the phase transition temperatures, T_g and T_i (Figure 7). Accurate identification of T_i is important because it determines whether

the mesogen alignment is in a nemetic phase or an isotropic phase based on Ti. T_i was identified as the temperature corresponding to the minimum point at the storage modulus, which was approximately 90-100°C (Figure 7 (a)). The glass transition temperature of was identified at the peak of the tan delta curve at approximately 20°C (Figure 7 (b)). In this study, we investigated the degree of alignment of mesogens in each temperature region as shown in figure 8 with applied mechanical strain simultaneously.



Fig 8. Schematic illustration of alignment of LCEs in the region between the phase transition temperatures, Tg and Ti. Both polydomain LCEs and monodomain LCEs become isotropic when the temperature is above Ti. In this study, we investigated the degree of alignment of mesogens in each temperature region with applied mechanical strain simultaneously.

3.2 Wide Angle X-ray Scatterings

WAXS analysis was carried out to observe the orientation of mesogens of thermo-mechanical LCE when deformed by temperature and mechanical force. WAXS method is commonly used for determining the molecular orientation because X-ray scattering pattern obtains the molecules direction. Therefore, the orientation of the mesogens can be analyzed by azimuthal intensity distribution of the mesogen direction (Figure 9 (a)). Using Full Width Half Maximum (FWHM), we could quantify the degree of orientation as a function of temperature and strain. As shown in the Figure 9 (b), the width corresponding to the one-half maximum intensity value is the value of the FWHM, and the more aligned mesogen molecules, the smaller the width of the FWHM[32].



Fig 9. (a) WAXS method used for determining the molecular orientation. X-ray scattering pattern obtained the molecules direction. The orientation of the mesogens can be analyzed by azimuthal intensity distribution of the mesogen direction. (b) Azimuthal intensity profiles of WAXS. $\Delta\beta$ is the FWHM of the distribution.

Since the WAXS intensity profile follows the Gaussian function, intensity curve was fitted with Gaussian function [33]. The degree of orientation was quantified by the

following equation 1.

Equation 1: Degree of Orientation (F) =
$$\frac{180 - FWHM}{180} \times 100(\%)$$

Figure 11, 12 and 13 show the WAXS images of polydomain and monodomain LCEs at each phase regions (glassy nematic, rubbery nemaic, rubbery isotropic) respectively with strained and without strained. For the quantitative interpretation of mesogen behaviors, the orientational behavior of mesogens was quantitatively established as a function of temperature and mechanical strain using FWHM.

3.2.1 Qualitative analysis

The mesogen behavior can be qualitatively analyzed by using WAXS image. When the alignment of the mesogen is oriented, the corresponding WAXS shows spotted shaped image while an isotropic distribution of mesogen molecules shows ring shaped WAXS pattern (Figure 10).



Fig 10. Representative WAXS 2D patterns of anisotropic and isotropic phase

3.2.1.1 Glassy nematic phase



Fig 11. Qualitative WAXS analysis of polydomain and monodomain LCE at 0°C (glassy nematic phase) without stretching and with 100% stretch

In the glassy nematic phase, mechanical stretch leads to the temporary aligning; therefore, originally randomly ordered LCE is getting ordered in one direction (Figure 11). When the temperature is lowered to 0°C from room temperature without stretching, direction of mesogens are still maintained as it was at room temperature. Temperature does not affect any of the alignment of mesogens in this phase.

3.2.1.2 Rubbery nematic phase



Fig 12. Qualitative WAXS analysis of polydomain and monodomain LCE at 50°C (rubbery nematic phase) without stretching and with 100% stretch

Rubbery nematic phase shows the similar ordering trend as glassy nematic phase. In rubbery nematic phase, mechanical stretch brings about an alignment of mesogens while the temperature is not a prominent factor to change the mesogens direction (Figure 12).

3.2.1.3 Rubbery isotropic phase



Fig 13. Qualitative WAXS analysis of polydomain and monodomain LCE at 120°C (rubbery nematic phase) without stretching and with 100% stretch

It was observed from figure 13 that the aligned mesogens are getting randomly oriented when the temperature is above T_i . In other words, in isotropic and rubbery phase, regardless of the mechanical stretch, originally randomly ordered LCEs are still in random phase. This implies that the temperature is a more dominant factor than the mechanical stretch to determine the mesogen ordering in this phase.



Fig 14. (a) Degree of Orientation of 100% stretched Polydomain LCEs as a function of temperature. Above Ti, orientation of mesogens is isotropic even though the mechanical strain is given. **(b)** Degree of Orientation of monodomain LCEs 100% stretched in director direction as a function of temperature.

Graphs for degree of orientation of LCEs when both the strain and the thermal energy are given as a function of temperature from glassy nematic phase to rubbery isotropic phase are shown in figure 14. The findings by WAXS demonstrate that in the range of temperature below Ti, no matter it is in the glassy phase or rubbery phase, degree of orientation for mesogens is less fluctuation. In addition to that, as the temperature approaches Ti, the change of degree of orientation influenced by thermal energy is greater than the mechanical strain. In other words, as the temperature is closer to Ti, temperature becomes a more dominant factor to determine the degree of orientation of mesogens. In this way, we assumed that there will be an inflection point of temperature at which the effect of temperature is more dominant in the direction of mesogen than that of mechanical force.

3.2.3 In situ WAXS analysis

For supporting the above WAXS results, we performed *in situ* WAXS analysis of monodomain and polydomain LCE. LCE sample was fixed at the tensile equipment. The initial distance between the two grips was 30 mm and the stretching rate was set at 100%/sec.

Figure 15 shows the intensity, Q vector graph of both poly and monodomain LCE at static state at different temperatures. The sample length was maintained at 30 mm while the temperature was increased. Polydomain LCE shows the same graph profile from room temperature to 150°C as assumed since initially randomly oriented mesogens are still randomly oriented when the temperature is above T_i (Figure 15

(a)). We need to take attention to the results of monodomain LCE at static state (Figure 15 (b)). We could notice that when the temperature is above T_i (100°C), the aligned monodomain LCE (100% stretched) becomes randomly oriented even though the sample is fixed with an initial distance. This means although LCE is 100% elongated at T_i state, LCE was randomly oriented. This supports the previous data that mesogen molecules behave randomly at isotropic state even under mechanical deformation.



Fig 15. LCE sample equipped at the tensile equipment at different temperatures (a) polydomain (b) monodomain

Subsequently we compared the mesogen alignment changes by temperature with LCE elongated by 100% and 150% (Figure 16). Based on Figure 16(a)(b), 100% elongated polydomain and monodomain LCEs present comparable results as mesogen molecules become randomly oriented above 100°C. This demonstrates that in isotropic phase, regardless of mechanical stretch, the orientation of mesogen becomes random. However, when both types of LCEs were stretched 150% (Figure 16(c)(d)), it appears that it is still aligned in an elongated direction even though the intensity got lowered than the temperatures below T_i . It was thought that the tensile speed was so fast at 100%/s that the mesogen molecules would follow mechanical forces before returning to a thermodynamically stable state. Therefore, after the stretching until 150% at 150°C, we maintained the elongation and observed the mesogen behavior for a minute. Figure 17 represents the mesogen behaviors as a function of time.



Fig 16. LCE sample strain, temperature *in situ* WAXS analysis (a) 100% elongated polydomain (b) 100% elongated monodomain (c) 150% elongated polydomain (d) 150% elongated monodomain



Fig 17. Change of mesogen behavior of 150% elongated polydomain LCE at 150°C as a function of time

Figure 17 indicates that mesogen molecules of 150% elongated LCE become randomly oriented less than a minute. This means, eventually, the mesogen acts erratically even with 150% elongation. Based on *in situ* WAXS, it gives more reliability of the mesogen behaviors when deformed by thermal energy and mechanical force. As the temperature approaches T_i , mesogen arrangement is dominantly changed by thermal energy while it dominantly changes by mechanical force below T_i . In this way, we assumed that there will be an reversal moment at which the effect of temperature is more dominant in the direction of mesogen than that of mechanical force.

3.3 Inflection temperature point

Stress relaxation experiment was also performed through DMA to identify the inflection temperature point where the change of degree of orientation of mesogens in LCEs gets more influenced by thermal energy than the mechanical strain. The change of direction of mesogens in LCEs is directly related to energy dissipation and absorption [34, 35]. Therefore, we came up with the idea of interpreting the alignment of mesogens in a mechanical way. The relaxation of the liquid crystal material consists of two stages: stress relaxation and orientation relaxation [36]. The first step is stress relaxation is the relaxation of polymer chains which occurs equally in both isotropic or anisotropic phases. The second step, orientation relaxation, is a relaxation that restores the mesogen to a thermodynamically stable equilibrium, which is only observed in anisotropic phase. It is believed that the presence of relaxation implies the presence of orientation relaxation. If the relaxation is not observed from the certain temperature, that means the intrinsic energy of mesogen provided by the thermal energy is big enough to prevent the relaxation. Therefore, it is able to find the inflection temperature point at which the temperature affects more dominantly than the given mechanical strain by scanning the presence of relaxation.



Fig 18. Stress relaxation curve of LCE1 resulting from the DMA test. Testing was performed under isothermal condition. (a) Stress relaxation curve of LCE1 at 0-65°C (b) Stress relaxation curve of LCE1 at 66,67,68,69°C. (c)(d) Stress relaxation curve of LCE1 at 70°C and 100°C respectively. Stress increase occurs clearly from the temperature 70°C. A short moment of relaxation tells the relaxation of soft segments that links mesogens, followed by the increase of stress implies the mesogen rotation is hindered by thermal energy. We could determine that the inflection point where the degree of orientation becomes more influenced by thermal energy than the mechanical strain is approximately 70°C.



Fig 19. Inflection point is approximately 70C revealed from the DMA stress relaxation test.

Stress relaxation test was performed at various temperatures under isothermal condition. Figure 18 (a) shows that the relaxation is observed until 65°C. Stress relaxation plots from the temperature 66 to 100 are shown in figure 18 (b)(c)(d). Stress increase instead of relaxation occurs from 70°C clearly (Figure 18(c), (d)). There is a sharp drop infers the relaxation of polymer chains that links mesogen monomers, followed by the increase of stress implies the mesogen rotation is hindered by thermal energy. Hence, the inflection point where the degree of orientation becomes more influenced by thermal energy than the mechanical strain was determined at approximately 70°C (Figure 19).

4. Conclusion

This study investigated the influence of temperature and mechanical deformation on anisotropic behavior of mesogen molecules of LCEs. We could quantify the degree of orientation as a function of temperature and strain. *In situ* WAXS analysis revealed that as the temperature approaches isotropic-nematic phase transition temperature, temperature becomes a more dominant factor to decide the direction of mesogen molecules than that of mechanical deformation. Dynamic mechanical analysis (DMA) was also carried out to identify the inflection temperature at various temperatures where the degree of orientation is more influenced by thermal energy through a relaxation test. Inflection point was determined approximately 70 °C. Based on this study, anisotropic behavior of LCEs by temperature and mechanical deformation was explored in laboratory, so that this provides a computational framework that accommodates microstructure evolution. Therefore, we could further develop mechanical, mathematical model capable of modeling the thermomechanical behavior of LCEs.

Appendix



Appendix A. In situ WAXS static WAXS pattern







Appendix B. In situ WAXS 100%, 150% elongated polydomain LCE WAXS pattern





Appendix C. In situ WAXS 100%, 150% elongated monodomain LCE WAXS pattern





Appendix D. *In situ* WAXS pattern of 150% elongated polymain LCE 150°C as a function of time

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Korean abstract

액정탄성체(Liquid Crystal Elastomer, LCE)는 유연한 고분자 사슬에 강 직한 이방성 액정 분자들(메소젠)이 약하게 가교결합된 고분자를 일컫는 다. 가교점에 의해 매우 높은 탄성력과 유연함을 가지는 LCE의 가장 큰 특징은 방향성과 위치성을 가진 메소젠 분자들이 외부 자극(열, UV, 전 기장, 자기장, 수분 등)에 따라 배열을 하게 되면서 이방적 거동을 한다 는 것이다. 또한 외부 자극으로 인해 메소젠 분자들의 질서도가 무너지 면서 메소젠 분자들의 방향성에 따라 가역적으로 LCE의 형상이 바뀌게 된다. 가역적 형상 기억 동작에 의해 LCE는 스마트 섬유, 4D 프린팅, 소 프트 스마트 로봇, 의료소재, 스마트 코팅 등 폭넓은 분야에서 적용되고 있다. 메소젠 분자의 배향에 미치는 주요 요소는 온도와 기계적 변형 두 가지이다. 본 연구에서는 LCE가 열과 기계적인 힘에 의해 변형될 때 메 소젠의 방향성이 어떻게 결정되는지를 광각 X선 산란(WAXS) 분석을 통 해 정량적으로 확인하고자 한다. Thiol-acrylate Michael addition 과 광 경화의 두 단계 방법을 사용하여 LCE를 제조하였다. WAXS 분석을 실 시하여 온도와 기계적인 힘을 주었을 때 합성된 LCE에서 메소젠의 이 방성 배향 거동을 관찰하였다. WAXS 분석 결과 온도가 등방성-네매틱 상전이 온도인 Ti에 가까워짐에 따라 배향도 변화는 기계적 변형보다 열에너지의 영향을 많이 받는 것으로 나타났다. 열에너지의 영향을 더 많이 받게 되는 변곡온도를 확인하기 위해 동적기계분석(DMA)도 실시 하고 완화시험을 통해 약 70℃의 온도를 구했다. 마지막으로 LCE에서 메소젠의 배향거동을 온도와 기계적 변형의 함수로서 정량적으로 확립하 고, 그 미세구조를 고려하여 LCE 변형거동의 역학적/수학적 모델의 개 발이 진행되고 있다.