Liquid Crystal Elastomers and LCE-Based Composite Material

Subjects: Polymer Science Contributor: Wei Zhang, Yifei Nan, Zongxuan Wu, Yajing Shen, Dan Luo

Liquid crystal elastomers (LCEs) are programmable deformable materials that can respond to physical fields such as light, heat, and electricity. Photothermal-driven LCE has the advantages of accuracy and remote control and avoids the requirement of high photon energy for photochemistry. An indispensable part of photothermally driven LCEs materials are photothermal materials.

Keywords: liquid crystal elastomer ; smart material ; photothermal-driven liquid crystal elastomers

1. Liquid Crystal Elastomers

Since Finkelmann et al. first reported liquid crystal elastomers in 1981, liquid crystal elastomers (LCEs) have under-gone tremendous development in both material chemistry and processing, becoming a class of materials with special properties ^[1]. Unlike liquid crystal polymers that are not crosslinked and liquid crystal networks that are highly crosslinked, low-crosslinked liquid crystal polymer networks (**Figure 1**a) with anisotropic polymer chains are known as LCEs ^[2]. Due to the low degree of crosslinking, anisotropic polymer chains can temporarily become isotropic when heated beyond the nematic-to-isotropic phase transition temperature (T_{NI}), resulting in contraction along the alignment (**Figure 1**b). At the same time, the degree of order in the LCEs is reduced with the loss of anisotropic chain conformation. The presence of the polymer network ensures that the LCE can obtain the original orientation when the temperature is lower than T_{NI} . This determines that the LCE undergoes reversible anisotropic deformation when the temperature changes. In fact, different application scenarios require LCEs. In general, the synthetic routes can be summarized into two groups: two-step crosslinking and one-step crosslinking. For the two-step cross-linking route, the LCE can be mechanically oriented because of the presence of a partially cross-linked polymer network. In the one-step crosslinking route, low molecular weight monomers are directly polymerized to form LCEs. Due to the low viscosity of the precursors, the LCEs prepared by one-step cross-linking are suitable for surface-induced orientation.



Figure 1. (a) Schematic of liquid crystal polymers, liquid crystal polymer networks and liquid crystal elastomers; (b) Schematic illustration of the contraction along the alignment of LCEs when heated beyond T_{NI} .

1.1. Two-Step Cross-Linking

The two-step crosslinking method proceeds in two steps, the first step forming a weakly crosslinked, partially reacted polymer network, whose shape and orientation can be easily changed. Through mechanical stretching and other methods, monodomain LCEs with the desired shape can be obtained, and the shape and orientation are fixed by the second-step reaction. A typical example of two-step cross-linking was presented by Finkelmann et al., which was based on liquid crystal polysiloxanes ^[1]. In the presence of a platinum catalyst, linear polysiloxane chains are mixed and reacted with vinyl liquid crystal monomers and multifunctional vinyl crosslinkers (**Figure 2**a). Taking advantage of the difference in the reaction rates of the two different cross-linking agents, the first-step reaction produces weakly cross-linked polymers, and aligns the polymer chains by mechanical stretching. Under the condition of weight loading, the second part of the polymerization reaction forms a strong cross-linked polymer network and permanently maintains a uniform director orientation.



Figure 2. Synthetic route for two-step cross-linked LCE chemistry. (a) Two-step crosslinking by hydrosilylation; (b) aza-Michael addition between diacrylate-based RMs and amines; (c) thiol-Michael addition of diacrylate-based RMs and thiols.

The two-step hydrosilylation reaction route relies on non-commercially available materials. Therefore, the preparation of LCEs based on the chain extension reaction of diacrylate-based reactive mesogens (RMs) is gaining popularity, including the aza-Michael addition method ^{[3][4]} and thiol-Michael addition method ^[5]. Because both of the above mentioned methods are based on purchasable liquid crystal monomers and other components, the initiation conditions of the two-step polymerization are orthogonal based on the chain extension reaction, enabling easy access and good controllability. For the aza-Michael addition (**Figure 2**b), a classic example is based on the chain extension of liquid crystal diacrylate monomers via aza-Michael addition with amines ^{[3][6]}, where the low viscosity of the reactive precursor and the slow reaction rate can be used for surface alignment ^{[3][7]}. The thiol-Michael addition reaction can be applied to chain extension to form oligomers (**Figure 2**c). After the alignment of oligomers, the orientation of the mesogens is then fixed by photopolymerization ^{[8][9]}.

1.2. One-Step Cross-Linking

Low molar mass liquid crystals have been studied for many years and are frequently used in daily life due to optical anisotropy and electrical tunability. Alignment techniques for low molar mass liquid crystals are well developed [10][11], which can also be used to align low-viscosity precursors of LCEs. Compared with the two-step cross-linking method, the low molar mass liquid crystal monomers are directly polymerized to form LCE in the one-step cross-linking method without the process of chain growth and partial cross-linking, which results in better maintenance of orientation. It is worth noting that this alignment technique is usually based on a treated surface, which possesses strong programmability, but the anchoring force weakens with distance. Due to the limitation of the anchoring force, LCEs fabricated by this alignment method are thin, and the LCE precursor is required to have a low viscosity. In the one-step cross-linking method, the polymerizable liquid crystal monomer, cross-linking agent, and initiator are directly mixed. Since no pre-polymerization process is required and the viscosity of the precursor is low, alignment can be induced by a surface to achieve spatially complex orientation. The first example of a one-step cross-linked LCE was synthesized by free-radical polymerization of acrylates [12]. Thomsen et al. used acrylate-functionalized LC monomers for crosslinking to obtain side-chain LCEs. Orientation was based on surface-induced orientation, where the material was poured into glass cells coated with a rubbed polyvinyl alcohol film, then cooled from the isotropic phase (95 °C) to the nematic phase (85 °C) at -1 °C/min to obtain a good orientation. This method only takes a few minutes to obtain LCEs, which saves time compared to two-step crosslinking.

2. LCE-Based Composite Material

An indispensable part of photothermally driven LCEs materials are photothermal materials. Photothermal materials can absorb light of specific wavelengths, transform photon energy into heat energy, and transfer the heat to LCEs for driving. The introduction of some kinds of photothermal materials can enhance the mechanical properties of LCEs as well. The research on photothermal conversion materials ranges from inorganic to organic, including carbon-based materials, metal nanomaterials, and organic dyes.

2.1. Carbon Based Material (CNT, Graphene, GO)

Carbon-based materials are generally commercially available and generally have excellent thermal conductivity and mechanical properties. Carbon nanotubes (CNTs) are cylindrical tubes rolled from graphene sheets. The diameter of the cylinders is generally nanometers, and the lengths are in the range of several micrometers [13]. CNTs have the ability to convert luminous energy into heat energy and exhibit high photothermal conversion efficiency, so they are a commonly used photothermal conversion material in LCEs [14][15]. As early as 2003, Courty et al. [16] reported a composite of CNT and LCE. At that time, the mass ratio of CNTs was very low, less than 0.02 wt.%, due to the incompatibility of nanotubes and polymers, which made it difficult to distribute them uniformly in the LCE matrix at high concentrations. In order to obtain higher photothermal conversion efficiency and mechanical properties, increasing the CNT concentration has become an important proposition. In 2008, Yang et al. [17] changed the surface properties of carbon nanotubes without changing their intrinsic properties to achieve high dispersion of single-walled carbon nanotubes (SWCNTs) in an LCE matrix, and achieved reversible deformation driven by near-infrared light. In 2010, Ji et al. [14] fabricated a pyreneterminated LCE to facilitate the dispersion of carbon nanotubes and the LCE was then stretched to induce CNT alignment with the orientation of the LCE so that well-dispersed and aligned CNTs were obtained. Based on the excellent photomechanical properties of LCE-CNT composites, they have potential for applications in various fields. For example, artificial light-driven Braille displays have been reported [18]. Benefiting from the strong photothermal conversion efficiency of CNTs, a sun-driven sunflower-like actuator was fabricated, which can effectively improve the working efficiency of solar panels [19]. LCE-CNT composites were also applied to fabricate light-weight soft robots to realize multi-modal movements of crawling, squeezing, and jumping ^[20].

As one of the most popular materials, graphene has also been incorporated into LCE-based composites. Like CNTs, graphene exhibits good photothermal properties in the near-infrared region. Yang et al. ^[21] reported that by arranging graphene sheets in LCEs, the graphene sheets can act as nanoheaters and trigger the phase transition of LCEs, thereby achieving a light-driven macroscopic deformation of up to 35.7%. Graphene has a tendency to self-aggregate, resulting in inhomogeneity of the composite. In contrast, graphene oxide (GO) contains oxygen-containing groups and carbonyl and carboxyl groups at the edges, so it is attractive for easy modification and dissolution. Li et al. ^[22] fabricated GO-LCE nanocomposite films that exhibited robust photo thermomechanical responses, reaching 33% uniaxial shrinkage and about 50% increase in payload actuation.

2.2. Metal Nanomaterial (AuNP, AuNR)

Photothermal metal nanomaterials, such as gold and silver, produce strong absorption when the incident photon frequency matches the overall vibrational frequency of the metal nanoparticle, generating a large amount of heat. This is a phenomenon produced by localized surface plasmon resonance (LSPR). The powerful photothermal effect provides a new approach for photothermally driven LCE. In addition to the photothermal effect, Montazami et al. [23] found that embedding gold nanoparticles (AuNPs) into LCE could improve the thermal conductivity, Young's modulus, and response speed of LCE. In this study, the response speed could be improved by more than 100%. Sun et al. [24] infiltrated micrometer-sized LCE cylindrical actuators with gold nanocrystals about 2 nm in diameter. The spatial translation, alignment, and rotation of the cylindrical microactuator were achieved by optical tweezers, and the bending deformation of the cylindrical microactuator was excited by a focused near-infrared (NIR) laser beam. Liu et al. [25] explored photothermal-driven LCE under visible light irradiation by dispersing gold nanospheres (AuNS) and gold nanorods (AuNR) directly in the LCE monomer. The LCE/AuNS and LCE/AuNR composites were accessed by UV curing, achieving a driving strain of 30% under 635 nm laser irradiation. Xu et al. [26] fabricated gold nanoparticles/LCE nanocomposites using 5 nm gold nanoparticles. The absorption band of the gold nanoparticles was about 475 nm to nearly 625 nm, occupying a major part of the sunlight spectrum, resulting in a photothermal-driven LCE that can be driven by sunlight. However, gold nanoparticles also have the problem of agglomeration. Wójcik et al. [27] used nanoparticles as a cross-linking agent for LCE materials to realize uniform dispersion in the LCE matrix and ensure good orientation of the LCE.

2.3. Organic Material (Organic Dye, PDA)

Compared with carbon-based composites and metal nanoparticles, organic materials are more likely to interact with LCE. Polydopamine (PDA) has attracted increasing attention because of its outstanding photostability and powerful photothermal effect in the near-infrared region. Tian et al. ^[28] used PDA to coat LCE films to fabricate optically responsive LCE films. By cleverly utilizing the property of PDA that can work in atmospheric and water environments at the same time, a bionic fish was manufactured that could swim on the water surface with NIR exposure. Lan et al. ^[29] made use of the rewritable properties of polydopamine coating to fabricate an LCE oscillator selectively coated with PDA. The powerful photothermal conversion ability of PDA allowed the LCE to be driven by sunlight, realizing the function of converting solar energy into electrical energy. Besides PDA, organic dyes such as disperse red have been widely used in LCE photothermal actuators and soft robots ^{[G][[2][30][30][31]}.

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