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An Analysis upon Various Applications of Nanoparticle-Liquid Crystalline Elastomer Composites: Synthesis and Characterization

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Abstract* – *This study focuses on recent developments in the field of liquid crystalline elastomers (LCEs) that bring these materials closer to the world of real applications, concentrating on their actuation properties. First, we briefly introduce different LCE materials that show actuation behavior and explain how they can be synthesized. In the second part, we focus on materials in which a shape change is triggered by a phase transition. In particular, we discuss how the chemistry of the polymeric material influences the strength and direction of the shape change. We review the efforts made to trigger the actuation event by stimuli other than temperature variation. Subsequently, we summarize preparation techniques for various sample geometries of aligned LCEs that all show actuation properties and assign them to particular applications. A short summary is given of devices that have been built in this way. In the third part, we concentrate on actuators that show deformation in an electric field without any phase transition. We start with a short introduction to ferroelectric liquid crystalline elastomers (FLCEs) and discuss molecules exhibiting these phases. Subsequently, we show how the electroclinic effect of FLCEs can be utilized to induce macroscopic deformations by an electric field.

Liquid crystalline elastomers (LCEs) are known to perform a reversible change of shape upon the phase transition from the semi-ordered liquid crystalline state to the chaotic isotropic state. This unique behavior of these "artificial muscles" arises from the self-organizing properties of liquid crystals (mesogens) in combination with the entropyelasticity of the slightly crosslinked elastomer network. In this work, micrometer-sized LCE actuators are fabricated in a microfluidic setup. The microtubular shear flow provides for a uniform orientation of the mesogens during the crosslinking, a perquisite for obtaining actuating LCE samples.

The thermal and mechanical properties of Liquid Crystal Elastomers (LCEs) were characterized using various techniques for understanding of their physical behavior. The material used for investigation was synthesized by us, using Finklemann procedure, with proper cross linking density in nematic phase. The material is found to have unique coupling between anisotropicorder of liquid crystal component and elasticity of polymer network. The chemical structures were confirmed by Fourier Transform Infrared (FTIR) Spectroscopy and Scanning Electron Microscopy (SEM). Fabry Perot Scattering Studies (FPSS), Thermo gravimetric Analysis (TGA) and Differential Scanning Calorimatory (DSC) were used to study thermal properties. The mechanical properties were studied using force sensor. Our investigation shows that this synthesized Liquid Crystal Elastomer has ability of spontaneous change as a function of temperature and mechanical force, which shows it as a unique class of soft material.

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INTRODUCTION

Liquid crystalline elastomers (LCEs) are materials that combine the properties of polymeric elastomers (entropy elasticity) with those of liquid crystals (self-organization). They are the subject of several reviews and books. Their most interesting property is the ability to change their shape reversibly after the application of a certain external stimulus. This feature was predicted by de Gennes as early as 1975. Since then, LCEs have been extensively discussed as materials for actuators. They offer an alternative to piezoelectrics, hydrogels, and various other types of polymer systems. The possible applications are wide, and range from micromechanical systems (in atomic force microscopy, as valves in microfluidic systems, as artificial muscles in robots) to propulsion systems (inspired by cilia in nature), and active smart surfaces that can change their properties according to the environment.

The basic idea behind the shape variation of LCEs is straightforward. Imagine a network swollen with an LC material. The polymer chains experience an anisotropic environment and deviate from the isotropic conformation. As a result, the coil dimension (the radius of gyration RG) will be different parallel and perpendicular to the LC director. Such an elastomer loses its anisotropy when heated to the isotropic phase. As a consequence, an isotropic chain conformation will be regained and the sample as a whole will change its shape. This scenario, which relies on the change of the order parameter S and the resulting anisotropy of the polymer chains, is used most often. Thereby, the change of the order parameter is either directly induced by a temperature variation or by an "isothermal" shift of the phase transition temperatures, which can be achieved by a photochemical isomerization of dyes.

Alternatively, an external (electric) field can be used to change the orientation of the LC director inside the network. The network will then reorient and produce a shape change. This effect can be observed either in LC actuators made from highly swollen nematic systems or in bulk LCEs with ferroelectric phases. In LCEs with ferroelectric phases, the electroclinic effect can lead to a change of the tilt angle of the mesogens in chiral smectic-C (smectic-C*) or chiral smectic A (smectic-A*) systems. This causes a change of the smectic layer thickness, which in turn induces the actuation. The polymer network serves here mostly as a matrix, which transforms a "liquid-like" ferroelectric phase into a "soft solid-like" ferroelectric, which can exert permanent stress. The magnitude of the shape change achievable in this way is smaller than for systems that rely on a nematic–isotropic (NI) phase transition. But, this actuation principle has the advantage that shape variations happen in direct response to an electric field (in fact it is a piezoelectric effect) and does not require heating.

LCEs can have different topologies depending on the attachment of the mesogenic units, which is important for the magnitude of the chain anisotropy. If they are incorporated into the main chain, a large interaction between LC phase and mechanical properties is expected. If the mesogens are attached as side groups (LC side-chain polymers), their orientation is decoupled from that of the polymer chains . Thus orientational correlations will be smaller than in LC main-chain polymers .

In this study, we will focus on the application of LCEs that can change their shape in response to temperature, to irradiation with light, or to electric fields (either by resistive heating or by a direct piezo-like response). Compared to inorganic piezoelectric materials, LCEs show a much larger shape variation but smaller forces. Compared to gels working by reversible swelling and deswelling, they have the advantage that the shape variation does not require mass transport of solvent. The basic principles of preparation and operation of LCEs – especially with regard to the route shown in Fig. 1a – have been described in . Still, some remarks concerning cross-linked liquid crystalline polymers seem appropriate in the present context. We will discriminate between LCEs and liquid crystalline thermosets. LCEs are a subclass of chemically (or physically) cross-linked polymers with a low crosslinking density, resulting in long polymer chains between the net points. Thus, they can be deformed easily to high strains and they swell strongly in good solvents. Typical elastic moduli (bulk state, above the glass transition temperature Tg) are in the range of megapascals. By contrast, highly cross-linked systems, so-called thermosets, are hard materials with little deformability that hardly swell. Their elastic moduli lie in the range of gigapascals.

Both types of networks can be made from LC polymers, depending on the amount of crosslinking agent incorporated. In addition, LCEs can be made by covalent crosslinking or by physical crosslinking due to the (reversible) segregation of hard or ionic blocks. Typical LCEs (low crosslink density) show NI phase transitions (e.g., clearing points) and a temperature-dependent LC order parameter. In LC thermosets (high crosslink density) the LC order is "frozen-in" and is nearly temperature independent, although photo isomerization can slightly change the order.

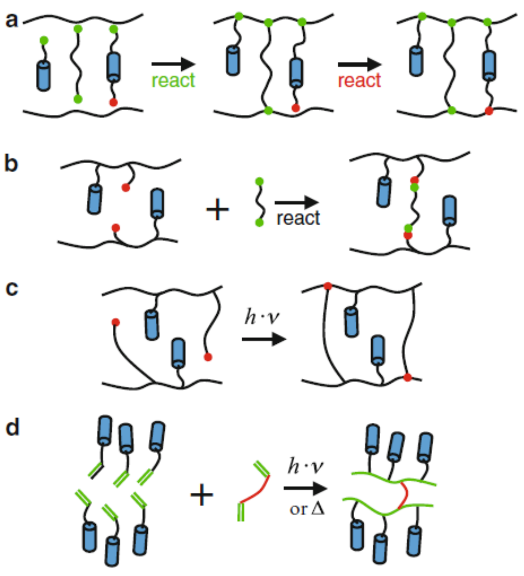

Fig. 1 Different reaction paths for the preparation of LCEs: (a) "One-pot" synthesis, usually via hydrosilylation; (b) reaction of LC polymer with a crosslinker; (c) LC polymer containing a reactive

group that is activated by UV irradiation; (d) mono- and bifunctional low-molecular-mass LCs that are polymerized

LCEs and thermosets offer differing potential applications. LCEs give rise to large deformations, which require a phase transition and strong deformability. The more densely crosslinked LC networks show small deformations, but their macroscopic shape variation can often be “boosted” by using bending deformations. In that case, tiny deformations at one side of an object can lead to huge bending deformations.

Liquid Crystal Elastomers (LCEs) are new class of soft materials which combine the elastic properties of polymers and orientational properties of Liquid Crystals. They consist of the cross linked polymer chain networks and the crystalline ordering of Liquid Crystal. Thus it introduces a coupling between the orientation of the me sogens and macroscopic elastic deformations of the network. LCE brings together three important properties: orientational order in amorphous soft materials, responsive molecular shape and quenched topological constraints, which helps to create many new physical phenomenon and have attracted significant interest from scientific community due to their fascinating thermal, mechanical, optical and electrical properties. The concept of LCE was put forward by the P.G Gennes, whereas, the first LCE was synthesized by Finkelmann. LCEs are divided into nematic, smectic and others depending on the LC phases exhibited by the systems. In nematic phase, the polymer chains elongate, while in the isotropic phase, they recover a random coil conformation, which is driven by their entropy.

In recent years the emphasis is being given on the synthesis and characterization of LCE. The studies of various physical stimuli, LCEs with thermo-responsive, photo-responsive and electro-responsive functions have been developed and LCEs as artificial muscles, micropumps and microvalves for microfluidic devices and optomechanical shutters have been actively explored -. Finkelmann et al. measured visco-elastic, opto-elastic and their behavior in electric field; Tajbakhsh et al. studied uniaxial monodomain Nematic elastomers. Terentjev et al. studied a wide range of photo sensitive materials; Dannio et al. studied thermo-tropic and elastic properties.

In one way or other, many new physical properties of these soft materials have been discovered -. In this work, we synthesized LCE using Finklemann procedure and the characterizations were performed by optical, thermal and mechanical techniques to understand the structure-property relation. These investigations confirm synthesis of LCE and the spontaneous effect on relative movement of their cross-linked end points results in the elastic response of the material which is very important for optimizing properties and achieving real applications.

Liquid crystal elastomers (LCEs) exhibit changes in their macroscopic shape due to the interaction of the mesogenic and elastic polymer components, exhibiting liquid crystallinity, elasticity and their interplay. Liquid crystal elastomers systems were created over 20 years ago and much of the thermal behaviour is understood well with thermally stimulated length changes of up to 400%. The major exploitable physical characteristic of LCEs, their unusually large thermo mechanical response, is driving numerous application-oriented activities.

One current problem, however, is how to create or reprocess LCE systems into a form that can be easily utilised whilst preserving the thermo-mechanical properties. In general, this requires the functionalization or addition of nanosized particles to instill properties in the LCE that can be altered rapidly by external stimuli. Various methods can in principle be used to induce changes in geometrical shape such as opto-mechanical, electro-mechanical or thermo-mechanical actuation. Opto-mechanical actuation directed towards direct optical to mechanical conversion can be performed through the use of photoisomerisable dyes, incorporated into the network. Mostly simple azobenzene dyes are chemically cross-linked, but they may also be dissolved into the network, liquid crystalline in nature, or even used as the cross linker. In general, the response time is on the order of minutes to hours, where the relaxation speed is similar and both are dependent on temperature. In polydomain LCEs, polarized light may also be used to control the direction of the shape changing response6 by selective adsorption in suitably aligned domains with respect to the optical polarization direction. How and where the heat is generated and whether it is significant in this process is still an open question.

Electro-mechanical actuation effects have been observed in ferroelectric liquid crystal elastomers7 and low molecular-mass nematogen-swollen LCEs. LC-like response times were observed, however with rather small elongational response.

Carbon nanotube/LCE composite materials9 can also be made electro-mechanically responsive, with a limitation of slow response times. More recently, by application of a high electric field across a smectic LCE bending motions have been induced by the electroclinic effect (direct coupling of molecular tilt in the smectic layer to applied field) with reasonable rates of response at relatively low voltages.

In thermo-mechanical actuation, the most simple solutions include the use of flexible conducting wires, optical absorption of light using a single sprayed adsorbing layer, or deformable conducting polymer plates that are resistively heated. Typically these types of approaches also have significant heat transfer problems, cause mechanical restriction as well as quick degradation due to large temperature gradients and mechanically incompatible parts. Carbon nanotube loaded LCE can also be actuated via opto-thermal compression of nanotubes. More recently, it has be shown that indirect heating mechanisms can be used, such as using LCE incorporating magnetic particles, where the magnetic field provides for vibration of the particles and creates local heating of particles in the LCE network.

LCES IN ELECTRIC FIELDS

Reorientation of the LC director in electric fields is the basis of liquid crystal displays (LCDs). Hence, it is straightforward to think of initiation of actuation in an LC elastomer by application of an external electric field that causes reorientation of the LC director inside the elastomer. This should lead to a reorientation of the anisotropic polymer chain which, in turn, induces a shape variation.

However, all experiments performed so far demonstrate that it is not possible to transfer enough energy for a shape variation on the nematic director. Because the network topology stabilizes the sample shape and chain anisotropy present during crosslinking , the director of nematic LCEs cannot be switched in electric fields if the shape of the elastomer is kept fixed. By contrast, for freely suspended and highly swollen pieces of nematic LCEs, shape variations in electric fields have been observed as a response to the reorientation of the director. However, the interaction with an electric field is much stronger for ferroelectric (chiral smectic) liquid crystals. It is possible to prepare ferroelectric LCEs in which a full switching of the director by external electric fields occurs while, at the same time, the director orientation present during crosslinking is stabilized by the network.

A second possibility exists for inducing a shape variation in ferroelectric LCEs. It results from the phase transition between a smectic phase with an orientation of the director along the layer normal (sA) and a smectic phase with tilted mesogens (sC*). This transition can be induced by an electric field (electroclinic effect) and leads to a decrease in the thickness of the smectic layers, resulting in a shape variation.

Ferroelectric Liquid Crystals and Their Networks - We will first describe LC phases with ferroelectric properties and subsequently outline the general properties of the ferroelectric LCEs (FLCEs). The most intensely studied phase is the chiral smectic-C* phase (sC*). It is the chiral modification of the smectic-C phase, a tilted smectic phase formed from chiral (pure enantiomers) rod-like mesogens. Chirality is essential because it eliminates the mirror plane present in the classical smectic-C phase. This reduces the symmetry of the phase and allows a macroscopic polarization perpendicular to the plane of the layer normal and the director, which now follows the average tilt direction of the mesogens. This macroscopic dipole moment (spontaneous polarization) is a consequence of the reduced symmetry and the fact that the lateral dipole moments of individual mesogens no longer cancel each other due to a slightly biased rotation around their long axis. This symmetry argument applies to all tilted smectic phases formed by chiral rod-like mesogens. However, for higher-ordered smectic phases than sC*, ferroelectric switching, which is the final proof of Ferro electricity, is difficult to perform due to the high viscosity. This problem is even more severe for FLCEs, in which the switching times can be very long .

Preparation of FLCEs - The outstanding property of FLCEs being their macroscopic dipole, the preparation must assure uniform alignment of the mesogens. The most direct approach to achieve this goal is application of an electric field during the crosslinking process . Because the material has to be aligned prior to crosslinking at elevated temperatures, thermal reactions are inapplicable and photo initiation becomes the method of choice. However, some photinitiators can give ionic impurities if irradiated in the presence of an electric field. Such a side reaction renders the sample unsuitable for experiments with electric fields.

Electromechanical Properties of FLCEs - In this section we discuss the properties of FLCEs that are important for applications. Two options are possible: either a mechanical deformation generates a change of size or orientation of the polarization of the FLCE (an electric signal), or an applied electric field generates a deformation. In the case that an electric signal is detected, the piezoelectric constant is obtained. If the sample is deformed, the generated strain is of interest.

NANOPARTICLE-LCE COMPOSITES

Smart materials, which are capable of converting external stimuli into mechanical responses; have long been recognized as an exciting and high-impact research area with widespread applications.

Several different types of responsive materials have been developed so far, with varying mechanical properties and response mechanisms. Of these, liquid crystal elastomers (LCEs) are a particularly useful and interesting class of materials that combine softness, elasticity, durability, light weight, high force density, and notable mechanical strength with dramatic reversible actuation. They have been studied as valuable candidates for artificial muscles for some time, and they also exhibit interesting potential as motors, contact lenses, micro grippers in microsystems, valves for microfludics and tunable lasing media.

In simple terms, LCEs are weakly cross-linked elastic polymer networks that incorporate rigid, anisotropic units (termed mesogens) bonded to the polymer chains. The mesogens can exhibit spontaneous orientational ordering, of the same type that is observed in ordinary low molar mass liquid crystals. However, since the mesogens are chemically bound to the cross-linked polymer network, any change in their orientation will be coupled to changes in the mechanical properties of the bulk material. If there is an overall preferred direction for the mesogens (termed the liquid crystal director) and this direction is the same throughout the material, then this network can be termed a mono-domain LCE (in contrast to a poly-domain LCE, in which each domain inside the material has a different director, see for a summary and details of poly-domain to mono-domain transition in LCE). As the mesogens undergo a phase transition from the liquid crystalline state to the isotropic state, mono-domain LCEs exhibit a significant change of their macroscopic shape due to the fact that motion of the polymer network is coupled to that of the mesogens bound to the polymer. The transition between the ordered and disordered states is dictated by the thermodynamic equilibrium; hence the shape change is fully reversible. After this phenomenon was originally predicted by De Gennes and experimentally confirmed by Finkelmann, theoretical and experimental studies in this area proliferated, driven both by scientific interest in this new functional soft matter (which combines both rubber-like elasticity and anisotropic liquid crystalline ordering), and by technological interest in the potential applications of such a material. Various types of LCEs have been developed. Uniaxial deformations of well over 300% (in the direction of the LC director) during the phase change have been demonstrated. LCEs also demonstrate other interesting physical features (such as soft elasticity, mechanical and electric instabilities) but it is this spontaneous reversible deformation—giving them a potentially large actuation stroke—that currently makes them stand out from other soft actuators.

The incorporation of nanoparticles into LCEs has been of considerable recent interest, with the aim of achieving a faster response speed and better control over the actuation. In most LCE systems, the large deformations seen can be achieved by heating the material, in order to trigger the LC change into the isotropic phase. However, the low thermal conductivity of polymeric LCEs prevents quick delivery of heat to all mesogens in the material, thus impeding the LC-isotropic phase transition—so that for thick and large LCE films, or indeed other shapes, the response time is an essential drawback for many applications. For practical applications, other drawbacks of direct heating are the difficulty of creating a heat supply that would change the surrounding temperature of LCEs at a very high speed, and the difficulty of creating a heat stimulus that would be entirely localized around the LCE component (so that adjacent actuating features could be stimulated independently). Even if such a heating mechanism were available, it would be difficult to incorporate it into a practical device. For easy manipulation of the actuating component, other stimuli (e.g., light, electric and magnetic fields) are far more appealing and it is with the goal of sensitizing LCEs to these stimuli in mind that researchers turn to the idea of incorporating other components into the material.

Since the underlying mechanism of actuation is the switching between the LC (in most cases—nematic) phase and the isotropic phase, in principle, any external source that could activate such a phase transition can be used to trigger the actuation. One strategy for sensitizing LCEs to an external energy source is to modify them with stimuli-responsive organic functional groups, either by covalently attaching these to the polymeric chains or by physically adsorbing them into swelling LCEs. Several photo-responsive LCEs have been developed by introducing photochromic groups into the LCEs. The majority of these photochromic molecules are azobenzene derivatives, although stilbene derivatives are also studied. Upon photo-irradiation with a suitable (UV) light source, the azobenzene group undergoes a trans-cis isomerization; since the trans form is a rod-like LC mesogen, while the cis form shows no mesogenic behavior, this process can cause a phase change in the LC ordered material and hence a deformation in a mono-domain material. Using polarized light, movement can even be induced in un-aligned poly-domain LCEs, thus considerably simplifying the preparation process for these materials. The detailed mechanism has been investigated. Recently, photoresponsive main-chain LCEs with azobenzene moieties have been developed and more interesting work has been reported. However, these materials do have inherent limitations, connected to the penetration depth of light within the material; if light only penetrates the surface layer of the LCEs, then only the surface chromophores will receive the light stimulus and the material will bend rather than contract. To achieve contraction of the LCE, the film needs to be thin and the material needs to be exposed to light over a long time period (of the order of minutes to hours) in order to accumulate enough light energy . An alternative LCE modification involves the incorporation of ferroelectric mesogens (having a high dielectric anisotropy) in order to sensitize the LCEs to an electric field. These mesogens in side-chain LCEs can change their alignment in response to an external electric field, resulting in an electromechanical effect with response times that can be of the order of 10 ms. Bent core LCEs have been developed to produce giant flex electricity for microscale parasitic power generation . Toward this end, main-chain ferroelectric smectic LCEs were synthesized, with analysis of shear deformation and Ferro electricity. However, strong electric fields are necessary to produce actuation in ferroelectric LCEs, and the amplitudes of the resulting mechanical contractions are quite small.

Resistive joule heating provides an alternative approach to the control of LCEs using electrical stimuli. The most straightforward method is to embed wires into the LCE matrix. When an electrical field is applied, as an ohmic resistance, the wires generate heat. The increased temperature causes the mesogens to undergo a phase change and contract, as in the case of direct heating. However, the wires are stiff and can thus restrict the LCEs from undergoing a large deformation. This method also faces critical heat transfer problems. A thin layer of conducting carbon on the LCE surface has the same shortcoming, with loss of mechanical response.

Nanoparticles can be processed into a thin layer on the LCE surface or distributed homogenously in the bulk LCEs. Some systematic work has been done with carbon reprocessed LCEs, where the pre-formed mono-domain LCEs were swollen in a solution containing carbon nanoparticles; evaporating the solvent from this solution leaves a thin conducting carbon layer on the surface of the LCE. Such a layer allows resistive heating in an electric field, resulting in electrical actuation with little loss of mechanical response. The mechanism, processing, electro-thermo-mechanical properties, material degradation and accompanied piezoresistivity effect of carbon reprocessed LCEs have been extensively reviewed previously, and will therefore not be included here. Herein, we summarize recent advances in LCE nanocomposites, with reference to representative original publications including our own work. We will begin by discussing the selection of nanoparticles and LCEs available, and will subsequently describe the resulting thermal properties and actuation of the resulting nanocomposite materials. We restrict ourselves to systems where nanoparticles are incorporated into mono-domain LCEs with emphasis given to the problems encountered in nanocomposite preparation. The review concludes with some relevant challenges and perspectives of this field to stimulate further discussions on design, fabrication and performance, and research interest in these nanocomposites.

POLYMER-DISPERSED LIQUID CRYSTAL ELASTOMERS

The widespread use of polymers and elastomers in modern technologies strongly relies on the fact that they are relatively undemanding for moulding, reshaping and machining. In most applications, these materials are used as passive mechanical components. Only recently, smart soft materials with external stimuli-induced mechanical responsiveness have been developed. Among them, electro active polymers1, have been employed most extensively. Nevertheless, liquid crystal elastomers (LCEs) are becoming an increasingly strong competitor in the development of a new generation of actuator and transducer elements2, both for macroscopic devices, for example, artificial muscles, and micro- and nano-sized devices, for example, microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS). In these smart polymer materials, changes in the molecular orientational order, equivalently nematic order, are manifested macroscopically as deformation of specimen geometry. The control of nematic order and the consecutive morphing can be achieved by varying the temperature, either by contact heat conduction, indirect heating via electromagnetic radiation-absorbing nanoparticle inclusions, or by photo isomerization.

Among the more exciting prototype devices exploiting shape memory behaviour of LCEs are microfluidic valves, Braille readers, holographic gratings and artificial cilia. However, current LCE synthesis methods still lack easy implementation into larger scale production environment. The major obstacle is the microscopic size of LCE domains: although individual LCE domains possess shape memory, the sample as a whole is inert since conventional polymerization methods yield isotropic distribution of domain orientations. A crucial step of imprinting shape memory into a macroscopically-sized LCE specimen is, therefore, to instill permanent orientational alignment of domains, that is, an effectively ‘monodomain’ state with anisotropic physical properties on the macroscopic scale. Currently, the most efficient way to achieve this is thermal polymerization of a mechanically stressed, partially cross-linked network. Unfortunately, this procedure allows neither for preparation of samples of arbitrary shapes, nor for the miniaturization and templating of the geometry.

An alternative method that omits partial crosslinking has recently been invented, but the alignment of domains still needs to be performed mechanically. Mouldable LCE materials for production of macroscopically sized monodomain parts of arbitrary shapes, that is, bulk parts with anisotropic thermo mechanical properties, thus remain rather elusive.

The availability of such materials could considerably expand the application scope of three-dimensional (3D) printing technologies, which currently rely almost exclusively on isotropic raw materials. Moreover, shape-programmable 3D soft objects could be fabricated through imprinting spatially inhomogeneous thermo mechanical or photomechanical anisotropy via curing in the presence of gradiented or vowelized (individually adjusted to small volume elements) non-mechanical external orienting field, using conventional fused deposition modelling and stereo lithography additive technologies. For two-dimensional (2D) elastic objects, the concept of programmable shape-changes has been demonstrated experimentally in thin elastic gel sheets with no uniform shrinkage properties and in LCE films with voxelized nematic director field25, as well as explained theoretically in terms of non-Euclidean metrics-driven out-of-plane curving of planar sheets exposed to external stimuli. Poor choice of suitable materials has so far impeded the extension of this concept to 3D.

In this paper, we present a new composite material, polymer-dispersed liquid crystal elastomer (PDLCE) that overcomes the above restrictions: it provides for moulding of soft elastomeric bulk or miniature, thermally morphable parts of any given shape. The main idea is to dope a conventional elastomer like polydimethylsiloxane (PDMS) with LCE microparticles (mLCEs). Used as fillers or inclusions in a soft polymer matrix, mLCEs render the composite material effectively thermomechanically active, provided that their axes of anisotropy are at least partially aligned. The latter is accomplished by curing the mixture of polymer resin and mLCE in external magnetic field, exploiting the diamagnetic anisotropy of the mLCEs29. Since these are small with respect to the size of the composite specimen, in homogeneities in local stress and strain can be disregarded, and the composite's effective elastic and thermomechanical properties resemble those of a conventional bulk, oriented LCE material. Unlike in competing approaches, macroscopic thermomechanical anisotropy is imprinted into PDLCEs without mechanical stressing, using external orienting magnetic field, which imposes no restrictions on the shape and size of the specimen. In contrast to currently prevailing efforts of designing LCE composites where LCE is used as the matrix, functionalized with micro- or nanoparticles, in PDLCEs it is mLCEs themselves that have the role of the colloid. We demonstrate that this paves the path towards designing thermomechanically functionalized conventional elastomers with tailorable shape memory and thermal expansion behaviour.

LIQUID CRYSTALLINE ORDER IN NETWORKS

In 1969 Pierre de Gennes was pondering the question, which benefit might come from the combination of liquid crystals and polymers, imagining an analogue to glass with enhanced elastic properties. It took a couple of years and some experiments before he proposed a unique feature of such a material: the use of liquid crystalline elastomers (LCEs) as artificial muscles. These would create macroscopic motion and force due to processes on a microscopic scale and surpass the response times of by then known pHresponsive polymer networks.

Several characteristics of an elastomer network have to be considered, namely the type of LC polymers, crosslinking strategies of the LC polymers, sample preparation and the mode of actuation-triggering.

Liquid crystalline polymers - As implied above, the influence of the mesogens on the polymer conformation is strongly dependent on the manner of interaction and is considerably stronger if the mesogens are linked to the polymer via chemical bonds. The length of the spacer dictates the influence of the mesogens on the polymer chain conformation. Longer spacers weaken the coupling between mesogen and polymer, while short spacers increase the shape anisotropy of the polymer chain. Additionally, the position of the spacer with regard to the mesogens influences the chain anisotropy and consequently the shape-changing properties.

Liquid crystalline elastomers - Highly crosslinked networks of LC polymer chains (thermosets) permanently lock-in the liquid crystalline order of the mesogens. Here the mesogens lack the flexibility to rearrange upon the transition to the disordered isotropic phase and the LC order is preserved even above TNI. These dense and highly ordered systems are useless for any actuator application, but exhibit unique optical properties which makes them useful as retarder foils for LC displays, wherein they further improve the color contrast or the viewing angle. It is essential to increase the flexibility of the mesogens to enable efficient actuation. Slightly crosslinked LCE samples with elastic moduli of several megapascals (MPa) have to be prepared, with crosslinking being accomplished in two ways: either via the formation of covalent bonds or via physical interactions between the polymer chains.

Preparation of LCEs and their use as active devices - While the contraction or expansion of a film is a macroscopic process, it results from the microscopic reorientation of the mesogens and the attached polymer chains. Although liquid crystals self-assemble in the nematic or smectic phase, the director does not align uniformly throughout the sample. Without an external directing force, poly-domains form, with the director being randomly distributed in the elastomer network. When, however, such an external force is applied during crosslinking, the mesogens and hence the polymer chains align along one preferred direction and form a mono-domain sample. In the latter case the loss of orientation in the isotropic phase results in a directed macroscopic shape change of the sample.

Stimuli-responsive LCEs: Not only temperature dependent - As already mentioned, the phase transition of thermotropic liquid crystals is triggered by a change in temperature. This most-common actuation was exploited for most of the LCEs presented so far. Admittedly, when integrating LCEs in an active device, it is not advantageous to heat the whole device. Efforts have been made to induce the desired shape change by local heating of the LC-elastomer. Incorporating carbon black allows electro-thermal heating of the now conductive LCE with an electric current. Similarly, the introduction of iron oxide particles into the elastomer allows inductive heating with an applied alternating magnetic field.

CONCLUSION

LCEs have been under investigation for several years. These systems are unique because of the combination of order and softness. During recent years, several developments have evolved that bring them closer to application. One important achievement is the introduction of various stimuli like electric current and irradiation with light that can, in addition to heat, trigger the NI phase transition and thereby the actuation process. In addition, FLCEs have been made that can produce a movement in an electric field without any phase transition. These new stimuli allow direct addressing of the actuator without the need to heat the whole device.

The spectroscopic techniques confirm the synthesis whereas a thermal and mechanical characterization shows elastic and spontaneous nature of LCE. This is a unique property where a macroscopic shape change costs little elastic free energy. This spontaneous change of LCE leads to many applications such as thermo-mechanical actuators and artificial muscles. The control of optical birefringence of LCEs makes them suitable for optomechanical sensors and the fact that they are rather soft mechanically and still retain their shape as solids, makes them highly suitable for bifocal contact and intra-ocular lenses.

In summary, the field of LCE is still maturing in many ways. The interplay of rubber elasticity and mesogenic ordering allows many possibilities in system design through change of the constituent components (mesogen (nematic, smectic, ferroelectric), crosslinker (rigidity, phase behaviour, functionality.), their relative ratios (crosslinking density) or the even method of the network formation (imposed stress, shearing,.). The understanding of interaction of LCE with nanoparticles is still in its infancy. An effective use of the unusual properties displayed by orientational or positional ordering and elasticity has yet to be fully utilised and the field has an exciting future.

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