Abstract
In this seminar I will present composite material Polymer dispersed liquid crystal elastomers, which solves some of disadvantages of liquid crystal elastomes. Composite materials have incorporated temperature responsive liquid crystal molecules. Because of this they are mechanically responsive to temperature change and have shape memory.
1 Introduction

Liquid crystals have been intensively studied and used for technologies from electro-optical displays to biosensors. Their unique combination of crystal-like molecular order and liquid-like flow properties made all that possible. Combining properties of liquid crystals with elastic properties of polymer networks we can create new functional materials, which exhibit reversible shape changes. Those new materials are called liquid crystal elastomers (LCE)[1].

In 1968 a French physicist De Gennes was first to identify potential of coupling between liquid crystals and elastic polymer networks. He envisioned new materials called liquid crystal elastomers with reversible shape change [2]. First working sample with reversible shape change properties was made by Kupfer and Finkelmann in 1991 with their two step synthesis process [3].

Ever since the first experimentally observed thermomechanical response of liquid crystal elastomers, their potential commercial applications were discussed[1]. They were envisioned as artificial muscles, microfluidic devices, Braille display and much more. But none of this applications were commercially realized so far[1]. Main obstacle in their applicability is complicated synthesis process which limits the shape and quantity of the final product. New material called Polymer dispersed liquid crystal elastomers (PDLC), first reported in Ref.[4], solves those limitations and uses more convenient synthesis process. This process enables us to create thermomechanically active objects with possibility of spatially controlled direction of response, which results in more complex deformations (bend, cup, saddle).

In this seminar I will first explain the nature and properties of liquid crystals followed by a short presentation of elastomers. In the third chapter I will use properties of both materials, explained in previous chapters, to show working principles of liquid crystal elastomers. In the last chapter I will discuss problems that prevent LCEs from possible applications and present new material that overcomes those problems and has potential for future use in applications.
2 Liquid crystals

Liquid crystals (LCs) are organic materials that show ordering similar to crystals, but they can also flow like fluids. This intermediate state between crystal and liquid is called mesophase. Materials that are find in mesophase are called mesogens and their molecules are either rod-like or discotic. We can divide LCs in two groups, based on the mechanism that causes orientational ordering of molecules in mesophase[5].

First we have thermotropics, which have temperature dependent phase behaviour. Their mesogens have greater molecular polarisability along the rod axis which means there is greater van der Waals attraction between two rods when they are oriented parallel than perpendicular (Figure 1). Thus, pair of molecules have lower energy if they are parallel than if they are perpendicular. At low enough temperatures this will be the dominant ordering mechanism and mesogens will be parallel, but if thermal energy exceed energy difference between parallel and perpendicular orientation of mesogens then they will get disordered. Temperature when liquid crystals go from ordered to disordered state is called phase transition temperature[2].

![Figure 1: Representation of induced dipoles of both mesogens. First mesogen has induced dipole $p$ which induces a dipole in the neighbour mesogen $p'$. If mesogens are parallel (a) the dipole of the second mesogen is bigger than if mesogens are perpendicular (b). This results in a stronger attraction and lower free energy. Reproduced from [2].](image)

The other group of LCs are lyotropics which have concentration dependent phase behavior. If concentration is high enough then mesogens are more likely to be parallel, because this gives them more space to move and allows them to translate more freely. In this way they maximize the disorder of translation, increase the entropy which lowers the free energy. States with lower free energy are more stable, so mesogens prefer parallel orientation[2].

Until now I have presented a few different groups of LCs, but not all liquid crystals order in the same way. We know three basic mesophases: nematic, smectic and chiral (Figure 2). The simplest is nematic phase, where long molecular axes are oriented in the same direction, causing molecules to be parallel to each other. Direction to which the molecules are pointing is called the director $\mathbf{n}$. Because molecules are symmetric, we can not distinguish between directions up and down. This is the reason why the director $\mathbf{n}$ is a double headed vector. Additional ordering of mesogens happens in the smectic phase, where besides the orientational order of long molecular axes, also molecular centres of mass are arranged in parallel layers. Third mesophase is the chiral phase, where mesogens are nematically ordered, but the nematic director is helically twisted, perpendicularly to the long molecular axis[3].
Figure 2: Different phases of LCs. Smectic C and Smectic A, where mesogens are oriented in the same direction and molecular centers are arranged in parallel layers. Difference between C and A smectic phase is that in smectic C, mesogens are tilted with respect to layers and not orthogonal. In the nematic phase mesogens are oriented in the same direction, but do not form layers. Phase with zero order is called Isotropic phase and it appears when LCs are heated (thermotropics) or their concentration is low enough (lyotropics). In this phase mesogens are not oriented in any specific direction. Chiral phase, where nematic director is helically twisted perpendicular to the long molecular axis. Reproduced from [6].

2.1 Orientational order

As described above, mesogens in nematic phase are all aligned in approximately the same direction, which is represented with direction of the director \( \mathbf{n} \). However because of finite thermal energy, mesogens are not completely aligned with director. To describe the degree of alignment we define the order parameter \( Q_{LC} \), as

\[
Q_{LC} = \langle P_2(\cos \theta) \rangle = \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right).
\]  

We use average of second Legendre polynomial of cosines of angle \( \theta \), which is the angle between mesogen long axis and the director (Figure 3). Order parameter can take values between 1 and \(-\frac{1}{2}\). First describes state where all molecules are perfectly aligned with director \( \mathbf{n} \) (\( \theta \) is 0 or 180°) and second where all molecules are orthogonal to director \( \mathbf{n} \). In the isotropic phase, molecules are randomly oriented and thus \( Q_{LC} = 0 \).

Figure 3: (a) Molecular axes are not aligned with director \( \mathbf{n} \), but they are tilted for angle \( \theta \). (b) Second Legendre polynomial as function of angle \( \theta \). Function correctly represents symmetry of up and down molecular orientation. Angle \( \theta \) is equivalent to \( 180^\circ - \theta \). Reproduced from [2].
3 Elastomers

Elastomer or rubber is made out of polymer chains that are cross-linked into macroscopic network. Cross links are chemical bonds, that form between polymer chains. This ensures the elastic properties of an elastomer. With applied force, polymer chains will reconfigure themselves in the direction of applied force. Cross-links between polymer chains are resisting to applied force, because the network chains have minimal free energy in their original and not in their deformed state[7].

\[ f_{el} = \frac{\rho_p k_B T}{2} \left( \frac{\lambda}{\lambda}^2 + \frac{2}{\lambda} - 3 \right) \]  

This equation gives us free energy density for uniaxial, constant volume deformation, where sample of length \(L\) is stretched to length of \(\lambda L\) and \(\rho_p\) is the number density of cross-links. When the external force is removed this makes polymer network to recover to original state. Elastomers can recover to their original size, after being stretched to more than twice their size.

![Elastomer Network](image)

**Figure 4:** Left picture represents an unstressed elastomer, where polymer chains are entangled. When we apply some force, network reconfigure itself in more ordered state and elongates. Reproduced from [8].

4 Liquid crystal elastomers

Now that we understand the ordering properties of liquid crystals and basic elastic properties of elastomers, we will be able to understand how liquid crystals elastomers (LCEs) work.

LCEs are made out of elastomer(cross-linked polymer chains) and LC mesogens (nematic, thermotropic mesogens) incorporated in an elastomeric net. They can be attached to polymer chains at the side and form side-chain LCEs or they can connect two polymer chains to form main-chain LCEs (Figure 5).

State at which we cross link sample, will define relaxed state. In our case this will be when mesogens are ordered and polymer chains are approximately parallel (Figure 7). If we now heat the sample over phase transition temperature, LC mesogens will become disordered and entangle the polymer chains. Whole elastomer will shrink. Then, when liquid crystal elastomer will be cooled down, elastomer will go back to original, relaxed state and mesogens will order again. For bulk sample of nematic side-chain LCEs the change is typically around 50% reduction of length at phase transition temperature around 80 °C [6].

This extreme thermomechanical effect can only be seen in monodomain (well aligned samples), where the nematic director is uniform along the whole sample. Without very special precautions during fabrication, liquid crystal elastomers are always found in polydomain form. Entangled polymer chains restricts movement and orientation of mesogens. Small domains are formed, where few closes neighbours are aligned. Their nematic directors are randomly oriented over the sample[2].
To fabricate monodomain LCEs you need to apply an external field to help mesogens to overcome the resistance of entangled polymer chains. It is possible to use both electric and magnetic fields, but in both cases strong fields are required. For example magnetic field $B = 11.74 \, \text{T}$ is not enough to get the complete monodomain LCE\cite{6}. Another possibility is to use a mechanical field in a two-step synthesis process, pioneered by Finkelmann et al\cite{3}. In the first step LCE melt is partially cross-linked to form a gel. This partially cross-linked gel is then stretched, which results in orientational alignment of mesogens. This ordered structure is frozen with further cross-linking in the second step.
5 Polymer dispersed liquid crystal elastomers

Process described above is not practical for producing LCEs for possible future applications, since it must be preformed manually and it only produces a thin strip of sample in a limited quantity. Therefore it is reasonable to try finding a more practical production method.

Composite materials called Polymer-dispersed liquid crystal elastomers (PDLCEs) are believed to overcome most production problems described above. They are completely moldable, without size or shape limitations and have potential to be applied to current elastomer production processes[4].

As their name tells, materials are made out of liquid crystal elastomer micro particles (µLCEs) mixed in polymer matrix. Monodomain µLCEs have the same properties as bulk monodomain LCE and when they are mixed in polymer matrix, they will make the whole material (PDLCE) thermomechanically active. µLCEs can be produced simply by crushing down monodomain LCEs, but with this we do not avoid complicated production method. Therefore, it is better to use a partially ordered LCEs sample produced with one-step cross-linking process. In this process magnetic field is used to help orientate mesogens and get bigger domains. Produced sample has domains several µm in size and by crushing sample to particles smaller than domains, is possible to get monodomain µLCEs particles[4].

Figure 8: (a) Bulk LCE is crushed into µLCEs, which are mixed into a polymer matrix. Then µLCEs are oriented in the magnetic field and finally the polymer matrix is cross-linked. (b) When domains are similar to micro particles in size, we get µLCEs with some nematic order. Ideally we crush sample to particles smaller than domains to get monodomain µLCEs. Reproduced from [6].

To accomplish the best shape changing ability, µLCEs must have their nematic director aligned in same direction. This is archived with magnetic field (Alignment is achieved in few minutes at around $B = 1T$ and in few seconds at around $B = 9T$)[4].

5.1 Orientation with magnetic field

First we define the time dependant orientational order parameter of µLCEs.

$$Q(t) = \frac{1}{2} \int_{0}^{1} [3 \cos^2 \vartheta(t, \cos \vartheta_0) - 1] \cos \vartheta_0$$  (3)
Here we must note that this order parameter is not the same as in Eq. 1, where it describes alignment of LC mesogens. In Eq. 3 \( t \) is time, measured from beginning of alignment, \( \vartheta \) is angle between nematic director of a \( \mu \text{LCE} \) particle and the magnetic field and \( \vartheta_0 \) is \( \vartheta \) at \( t = 0 \).

At the beginning of the orientation, \( \mu \text{LCEs} \) are isotropically distributed (\( Q = 0 \)). When we turn on the magnetic field, diamagnetically anisotropic microparticles induce dipole and they start to feel the magnetic torque.

\[
M_B = -\frac{1}{\mu_0} V Q_{LC} \Delta \chi B^2 \sin \vartheta \cos \vartheta \tag{4}
\]

Here \( V \) denotes the volume of a microparticle, \( Q_{LC} \) nematic order parameter of the particle, \( \Delta \chi \) the anisotropy of the diamagnetic susceptibility. We can now write the equation of motion, in which we disregard the acceleration because we are at the low Reynolds number regime (\( Re \sim 10^{-8} \)) and use viscous torque for particles approximated with spheres.

\[
0 = -\frac{1}{\mu_0} V Q_{LC} \Delta \chi B^2 \sin \vartheta \cos \vartheta - 8 \pi \eta r^3 \frac{d\vartheta}{dt} \tag{5}
\]

If we introduce characteristic time

\[
\tau = \frac{6 \pi \mu_0}{Q_{LC} \Delta \chi B^2} \tag{6}
\]

and dimensionless time \( \hat{t} = t/\tau \) then Eq. 5 simplifies to:

\[
\frac{d\vartheta}{d\hat{t}} = -\sin \vartheta \cos \vartheta \tag{7}
\]

We can solve this equation with initial conditions \( d\vartheta/d\hat{t}(\hat{t} = 0) = 0 \) and \( \vartheta(\hat{t} = 0) = \vartheta_0 \) and get the analytical solution for \( \cos \vartheta \).

\[
\cos \vartheta(\hat{t}, \cos \vartheta_0) = \frac{1}{\sqrt{1 + \frac{1 - \cos^2 \vartheta_0}{\cos^2 \vartheta_0} e^{-2\hat{t}}}} \tag{8}
\]

This solution can now be inserted in Eq. 3 giving us the time dependant equation for the order parameter of microparticels.

\[
Q(\hat{t}) = \frac{\sqrt{\hat{t}^2 + 1} - 1(2\hat{t} + 3e^{2\hat{t}} - 3e^{2\hat{t}} \arctan \sqrt{e^{2\hat{t}} - 1})}{2(e^{2\hat{t}} - 1)^{3/2}} \tag{9}
\]

Now we can calculate the time needed for particle alignment. Desired alignment of \( Q = 0.9 \), will be reached in \( t = 3.1 \tau \). For our set of materials, with \( \eta \approx 3.5 \text{ Pa s} \), \( Q_{LC}(T_{room}) \approx 0.65 \) and \( \Delta \chi \approx 10^{-7} \), we find the time needed for orientation to be \( t(\text{B=1 T}) \approx 22 \text{ min} \) and \( t(\text{B=9 T}) \approx 17 \text{ s} \).[4]

### 5.2 Thermomechanical response

With PDLCE material described above is now possible to create shape changing samples of arbitrary shapes and different reshaping styles. To determine contraction response we use a long cylindrical sample (Figure 10). On Fig. 9 we can see thermomechanical response curves for different types of \( \mu \text{LCEs} \). Maximal response (reduction of length) of 12% is observed for \( \mu \text{LCEs} \) produced from monodomain side-chain LCE (PDLCE-A) and from partially oriented sample (PDLCE-C)[4].
Figure 9: Thermomechanical responses of PDLCE samples from monodomain (PDLCE-A) and partially oriented (PDLCE-C) LCE. Grey line represents thermal response of a clean elastomer (PDMS-Polydimethylsiloxane). Observed response is the same for both samples and is around 12%. Adapted from [4].

Figure 10: Sample used to measure thermomechanical response. Reproduced from [4].

5.3 Shape changing samples

PDLCE gives us a possibility to produce more complex samples where orientation of $\mu LCE$ can be spatially controlled. This results in arbitrary deformations of sample on temperature changes. This is shown on Fig. 11 where discs of various orientation director configurations are shown. Discs are made of two layers, each has $\mu LCE$ particles oriented in different directions. Bilayer disks exhibit different curved shapes in response to heat stimuli. Resulting shape depends on the orientation of both layers.

For example if the top layer has director in horizontal direction and bottom layer is not oriented, then upon thermal activation top layer will contract, while bottom layer will not. This will result in folding of a sample. On the other hand if the bottom layer has director in vertical direction and top is not oriented, we get a cup deformation. Orientation of both layers directors separated for $90^\circ$ angle in horizontal plane, will result in saddle deformation [4].

6 Conclusion

The combination of liquid crystals and elastomers gives us promising materials (liquid crystal elastomers), which exhibit thermomechanical response with around 50% reduction in length. This response is comparable with the strain of human skeletal muscles of $\sim 30\%$ [1]. This gives LCEs potential for many applications. Some prototype devices were already developed, such as microfluidic valves, Braille reader, holographic gratings and artificial cilia [4]. However, because of complicated synthesis methods LCE materials can not be produced in large quantities, so they are not suited for commercial applications. Because of this limitations, new composite materials (Polymer dispersed
Figure 11: On the top are models of bilayer samples with two sided arrows representing orientation director, blue arrows for top layer and purple for bottom layer. At the bottom there are pictures of samples at low (T=300K) and high temperature (T=400K). (a) Top layer is ordered horizontally (\(n_t \perp z\)) and bottom one is disordered (\(Q_b=0\)). This configuration results in folding deformation. (b) Bottom layer is ordered vertically (\(n_b \parallel z\)) and top one is disordered (\(Q_t=0\)). This configuration results in cup deformation. (c) Top and bottom layers are both ordered horizontally, but in perpendicular directions. (\(n_t \perp z, n_b \perp z, \Delta \varphi = 90^\circ\)). This configuration results in saddle deformation. Reproduced from [4].

Liquid crystal elastomers) were developed that enable producing arbitrary shaped samples with thermomechanical response of 12%. This is less than LCEs, but possibility of spatially orienting micro LCE particles in desired direction, gives material ability of shape memory. Simplicity of synthesis also gives us many potential practical uses of materials in 3D printing and additive manufacturing of devices with thermally activated shape memory.

References


