# Active Polymers for Renewable Functional Actuators (APRA)

Eugene Terentjev discusses his ERC Advanced Grant award APRA

Liquid crystalline elastomers (LCE) make a remarkable class of materials. At their inception in the 1980s,[1] LCE represented a mere curiosity, but two events in the early 1990s have turned LCE into one of the hottest topics of international multi-disciplinary research and development: Finkelmann (in Germany) started working with siloxanes, making the low glass transition elastomers (rubbery in the 'human' temperature range), and learned to make *monodomains* [2] (large samples with uniformly aligned orientational anisotropy). At the same time, Warner and Terentjev have developed a complete theory of LCE state and mechanics [3]. After this, meaningful experiments on LCE with controlled alignment became possible – and the good theoretical understanding of the processes guided these studies. As a result, the field has 'exploded', and today there are dozens of strong research groups in EU, USA, Japan, China, Russia, India, Brazil, Mexico, etc. publishing hundreds of research papers a year. The 16th biannual International Conference on LCE took place in Houston, 2017, with several hundred participants, with a programme solidly focused on LCE applications.

One of the two key theoretical predictions about LCE was their '*equilibrium actuation*' (the other being the '*soft elasticity*': an equally remarkable topic, also promising many unexpected applications). Finkelmann has soon confirmed

this effect [2,4], and then a systematic study of Tajbakhsh and Terentjev [5] has established how the degree of microscopic polymer chain anisotropy affects the spontaneous and fully reversible change of sample length. This elongation ratio L/L_0 is called the 'actuation stroke', and the illustration shows that it changes continuously in proportion to the temperature change below the isotropic transition point, with the maximum stroke of 50% for the lowest curve – and up to 250% for the highest curve (the materials in that study [5] differed in the fraction of added main-chain polymer, increasing the average local anisotropy; this change also shifts the isotropic transition point). In order to evaluate mechanical work done by such an actuation cycle (heating-cooling in this case), there has to be a load (stress) applied, and the illustration shows one representative LCE doing mechanical work of ~150 kJ/m^3 per unit volume (evaluating the full work would be misleading, because *W=force*displacement*, and the displacement depends on how long the initial sample was: you can have as large work *W* as you want by lifting the same weight by a longer strip of LCE). Our long experience with LCE tells that these materials can only withstand the maximum stress of ~100 kPa before breaking (both in tension and in compression), so the maximum mechanical work per unit volume cannot exceed ~50 kJ/m^3 for an
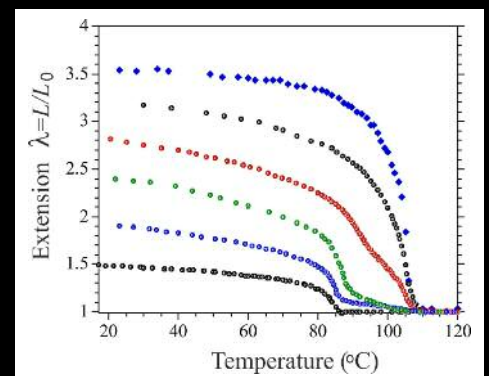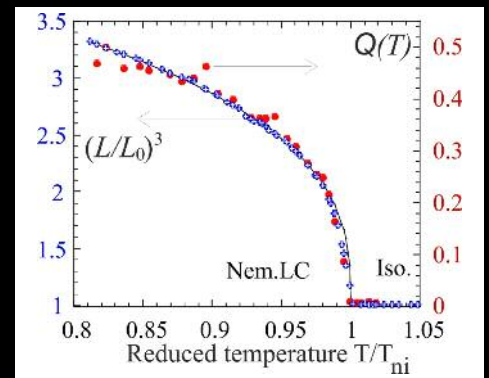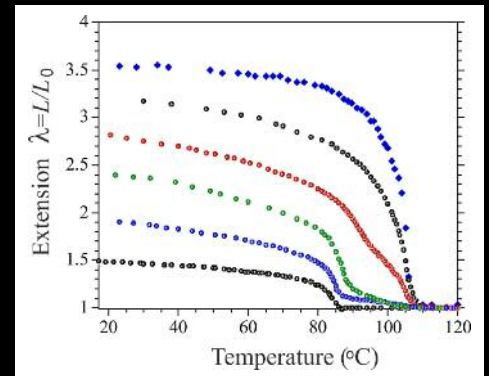
elastomer with a 50% actuation stroke as an illustration. It is important to emphasize the equilibrium nature of LCE actuation: it is the natural length of the sample that is changing, and so the process can repeat over as many cycles as needed – it is only the applied load that may lead to degradation.

It is also important to note that the majority of modern literature on LCE actuation is focused on bending (rather than linear tensile tests described above). For the simple reason: in bending, when one side of the sample contracts with respect to the opposite, one can achieve a very large amplitude of motion by very little input; the mechanical work in such a bending cycle would be close to zero. So many spectacular results on bending actuation [6] are perhaps interesting for signal guidance, or surface reflectance – but certainly not for any mechanical application.

The Warner-Terentjev theory makes it clear that the reason for mechanical actuation is the change in the orientational order of molecules, which are well-aligned (monodomain) and are crosslinked into a dense network. Both Finkelmann and Terentjev have quickly realised that one can change this order not just by changing the ambient temperature (as people do in ordinary liquid crystals), but also by light – if the molecules making the network contain

photo-responsive groups [7]. This started a new wave of excitement in LCE actuators: now you could induce a large mechanical action fast, and without contact, just by shining a light on the elastomer [6,8]. There are two mechanisms behind *photo-actuation*: a direct release of heat on light absorption, which causes local change of orientational ordering for entropic reasons – and a more delicate effect when the photo-absorbing molecule is an anisotropic rod itself, and undergoes photo-isomerisation disrupting local orientational anisotropy (azobenzene derivatives) by altering the potential energy of anisotropic interaction. Initially the two were confused, but later these mechanisms were clearly separated [9], and now a much preferred (far more robust) method is the first: one can select specific dyes that are more efficient in releasing heat, and absorb in a required spectrum range, and disperse them in the LCE actuator to enable its photo-response. Our long experience shows that carbon nanotubes and graphene nanoplatelets are the best in converting broad-spectrum light into local heat – while the laser welding dyes like isocyanine green are best to convert narrow-band near-infrared light into high local heat [10] (while azobenzene derivatives have a narrow-band UV absorption [7]). The illustration (data from [10]) shows the 'light ON' – 'light OFF' cycles on a typical LCE doped with a standard commercial dye (not optimised for the photo-actuation), pointing the repeatability of response, and the dependence on light intensity. The speed of response has been shown to be determined by the rate of absorption saturation in a material (faster in thinner samples), and could be made to fractions of a second.

The speed of actuation response, the magnitude of actuation stress (on length-fixed sample) and the stress-strain-power values make LCE the material that matches the human muscle parameters almost exactly. The illustration of 'Actuation Map' (from a review [11]) shows where
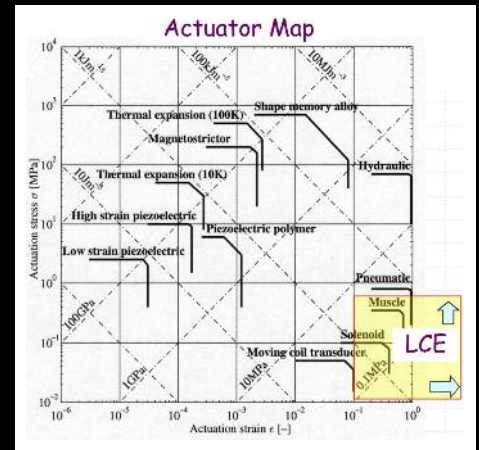
the range of LCE actuators sits comparing to many other systems used in technology. The ability to initiate the mechanical action by light adds to the attractiveness of the material; other stimuli (i.e. methods of changing the local orientational order) have also been demonstrated – by solvent intake or by magnetic heating when ferrous nanoparticles are dispersed. However, all these effects rely on the fact that LCE is formed as a monodomain – and since Finkelmann's work there is no other practical method to form a uniformly aligned crosslinked elastomer than by his two-step crosslinking process [2,4].

The two-step crosslinking-alignment process relies on the separation of time scales. Once the polymer solution is prepared, crosslinking is initiated and the system is allowed to form a weak gel. Once in this state, a mechanical deformation is applied (usually a uniaxial tensile stress), during which the polymer chains that are already crosslinked develop a specific uniform stress-induced anisotropy. At this point the final full crosslinking is applied 'freezing' this anisotropy in the network. Unfortunately, this two-step process fundamentally cannot produce anything except a flat strip (or a thick fibre): the weak gel at the first stage does not permit complex shape formation – if that first stage is carried to a stronger gel, then no good LCE alignment and actuation can occur, because it is the non-crosslinked chains that will be made in anisotropic conditions and lead to the
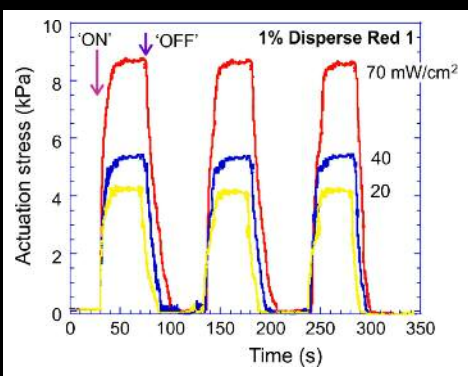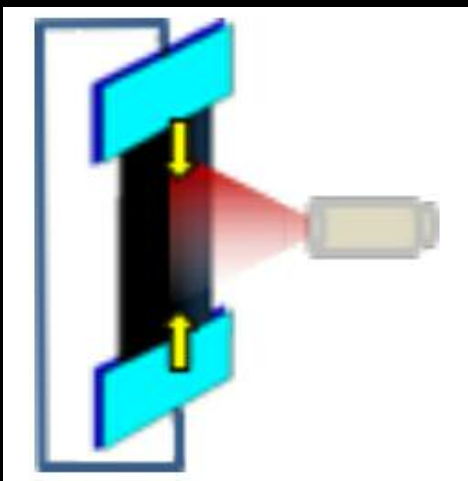
final order and actuation. This 'bottle-neck' is the reason why there are no spectacular applications of LCE on the market. This is where the field is now: LCE offer a great promise, remarkable opportunities – yet for a technical reason their best applications remain practically non-viable.

The APRA project aims to change this status quo, and open the road for these new applications.

We always understood that an alternative solution to the 'two-step crosslinking' protocol was needed, which could only come from a concept of *thermoplastic elastomers*: networks that are crosslinked dynamically and that could be re-moulded at a high temperature into complex shapes. All modern polymer industry uses this thermoplastic concept: from shoes to aircraft. We have tried many things over many years, and grew to understand that it cannot work. The reason is that for actuation we need to release a lot of heat internally, which inevitably disrupts the thermoplastic matrix and undermines the mechanical strength of the material: fundamentally such actuators will show creep after many cycles.

So when Ludwick Leibler (ESPCI, Paris) has announced their new idea of *vitrimers* [12], we knew this is our 'ticket'. Unlike in usual thermoplastic networks, which have their dynamic crosslinking increasingly disrupted on heating, in a vitrimer the number of covalent bonds holding the network together remains constant at all times. But the rate of a bond-exchange reaction (BER) increases on heating, in a very sharp manner since high energy barriers are involved, which allows the material to become malleable: easy to pressure mould above the 'vitrification temperature' Tv (which is often 130-180°C or could be higher). Yet the

differential stiffness and the structural integrity are not compromised, since the crosslinking bonds exchange their connectivity, but do not reduce in number. We followed Leibler's ideas and formed such BER polymer networks with liquid-crystalline (rod-like) molecules – and named these liquid crystalline vitrimers xLCE, for '*exchangeable LCE*' [13].

Project objectives are divided into two distinct parts: Part A is the chemistry-led element, where we will work to optimise the new xLCE structure for each target application. It needs a lot of innovation in itself, and several major challenges to face, but its ultimate role is to provide a sufficient amount of photo-actuating xLCE material with required parameters for the use in target applications. Part B is the device-engineering element of this project. There are several different representative applications, which form the five tasks of Part B – yet it is likely that in the course of this project new ideas would turn up, internally or from outside, and we will do something else as well.

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PROJECT SUMMARY

This project will bridge from the concept to technology, tuning the material design for robust nematic LCE vitrimers, imparting photo-actuation capacity with a controlled wavelength, and finally utilising them in practical-engineering actuator applications where the reversible mechanical action is stimulated by light, solvent exposure, or more traditionally – heat.

PROJECT PARTNERS

The APRA Project is coordinated from the University of Cambridge.

PROJECT LEAD PROFILE

Eugene Terentjev studied in Moscow, obtaining the MSc in 1982 and PhD in 1985; then carried out postdoctoral research in Case Western Reserve University (Cleveland, Ohio). After moving to Cambridge in 1992, he became a University Lecturer in 1998 and Professor of Polymer Physics in 2005. Professor Terentjev authored over 300 original papers and reviews in a broad range of subjects in soft matter and biological physics.

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