

Heliotracking device follows beam of light

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Liquid crystalline elastomers (LCEs) make a remarkable class of materials, with most attention currently focused on their application as actuators and artificial muscles (Warner and Terentjev, 2007). The APRA project has its main focus on the further development of these LCE actuators, utilising the 'dynamic networks' concept (Montarnal *et al.*, 2001), thus making the elastomers malleable at high temperature. This allows the moulding of complex actuator shapes, 3D printing of LCEs, and, importantly, full recycling and re-configuration of the material into new shapes. This article introduces these 'exchangeable LCE' materials (xLCE) across a broad spectrum of chemistries.

Dynamic liquid crystal networks

The idea of a large-strain reversible mechanical actuator based on the intrinsic material properties of LCEs has been understood for over 30 years (Küpfer and Finkelmann, 1991). The key characteristics of LCE actuation are remarkable: fully reversible action, large amplitude, with a stroke of up to 500 per cent (Ahir, Tajbakhsh and Terentjev, 2006), and the stress-strain-speed response matching or exceeding the human muscle. The origin of this effect lies in the direct coupling of the macroscopic shape of a cross-linked network and the underlying anisotropic order of its polymer strands. For example,

the length of a sample contracts along the director axis when the internal liquid crystal order is altered by heating into the isotropic phase (although other ways of altering the order parameter exist, extensively reviewed in the literature), the macroscopic shape of elastomer changes in a reversible and equilibrium way (Warner and Terentjev, 2007). At the same time, separately from the natural order–shape connection leading to actuation, LCEs have a unique mechanical property of 'soft elasticity' (when elastic deformation may occur at low or zero stress), which leads to a different strand of potential applications (Clarke *et al.*, 2001; Ohzono *et al.*, 2019)

Mechanical stretching via two-step cross-linking was the first technique to achieve the permanent uniform molecular alignment in LCEs. This achievement has 'ignited' the whole field of LCE research and applications. Küpfer and Finkelmann (1991) utilised a two-step reaction to enable the stress-aligning of the weakly cross-linked LCE gel between the steps, based on different reaction rates. A fast hydrosilylation reaction was used to attach side-chain vinyl mesogens to a siloxane backbone in the first step. The second step was to cross-link the network via a much slower reaction of siloxane with acrylate cross-links, the long window of time to full cross-linking allowing for the mechanical stretching and aligning of the gel. The second

reaction was allowed to complete in the sample under load to lock in the newly aligned conformation. This technique has been extensively used by many research groups, for many years. However, this method suffered from fundamental problems, which restricted the real-world applications of LCE materials. The difficulties originated from the lack of control over the reaction kinetics during the alignment step: applying the load too soon to a still weak gel results in fracture, while applying the load too late in the continuously ongoing cross-linking process results in poor alignment and strong random disorder.

The concept of LCE networks cross-linked using dynamic covalent bonds appears to solve these limitations by allowing the elastomers (thermosets) to be processed after full cross-linking. The aim of re-processing is to gain access to well-developed methods used in the thermoplastic industry—extrusion, fibre drawing, and injection moulding (Montarnal *et al.*, 2001). Dynamic polymer networks are malleable through topological rearrangements at high temperature and under stress (Winne, Leibler and Du Prez, 2019). In the case of an exchange reaction with an associative mechanism, the total number of covalent bonds and the network integrity remain constant throughout the plastic deformation. For dissociative bond exchanges (and equivalently in

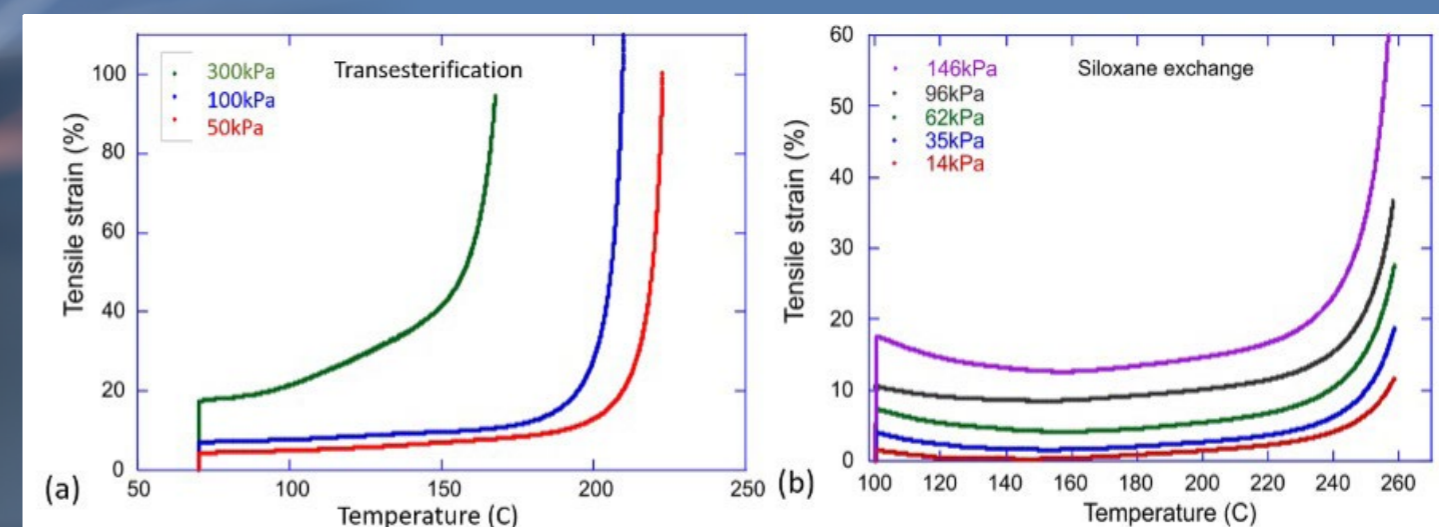


Figure 1: An illustration of elastic-plastic transition in xLCE. a) The iso-stress heating curves for a dynamic network controlled by transesterification. b) The iso-stress heating curves for a dynamic network controlled by equilibrium siloxane exchange.

physically cross-linked materials), the bond dissociation leads to a drop in viscosity during the process, though in the long term, the mechanical properties are partially or fully recovered through bond reformation. This contrasts with standard thermoplastics, which melt on heating, retaining no structural integrity.

Various stimuli can be used to activate the bond exchange: thermal, light, or chemical (such as pH). For example, bond-exchange reactions that can be thermally activated include the Diels-Alder reaction, the thiol-Michael adduct dynamic equilibrium, urea-amine exchange, transesterification, transcarbonylation, transcarbonation, thiourethane bond exchange, vinylous

urethane-amine exchange, siloxane exchange, and others. Examples of light-activated reactions include addition-fragmentation chain transfer, cycloadditions, and others. There are several examples of multi-stimuli activated bond exchanges (e.g. light + temperature), such as with disulfides, cycloadditions, or boronic esters. Choosing the right stimulus to trigger the bond-exchange reaction is very important, as it dictates the processing conditions and the subsequent applications of the LCE networks. For instance, elastomers cross-linked with thermally activated exchange must be processed (aligned, reshaped, welded, and recycled) at high temperature, which means in the isotropic state. On the other

hand, LCEs cross-linked by light-triggered exchangeable bonds can be processed at low temperature in the nematic state.

The ability to mould and program xLCE shapes allows us to weld different materials (with different transition temperatures) and form actuator shapes that are strong and resilient. Figure 3 illustrates one such actuator shape and the repeated cycles of contraction and expansion on heating/cooling of the sample. Our ability to tune the chemistry allows the temperature of the main actuation stroke to be chosen between quite high (as in Figure 3) down to room temperature when the large length change is induced by the heat of a hand.

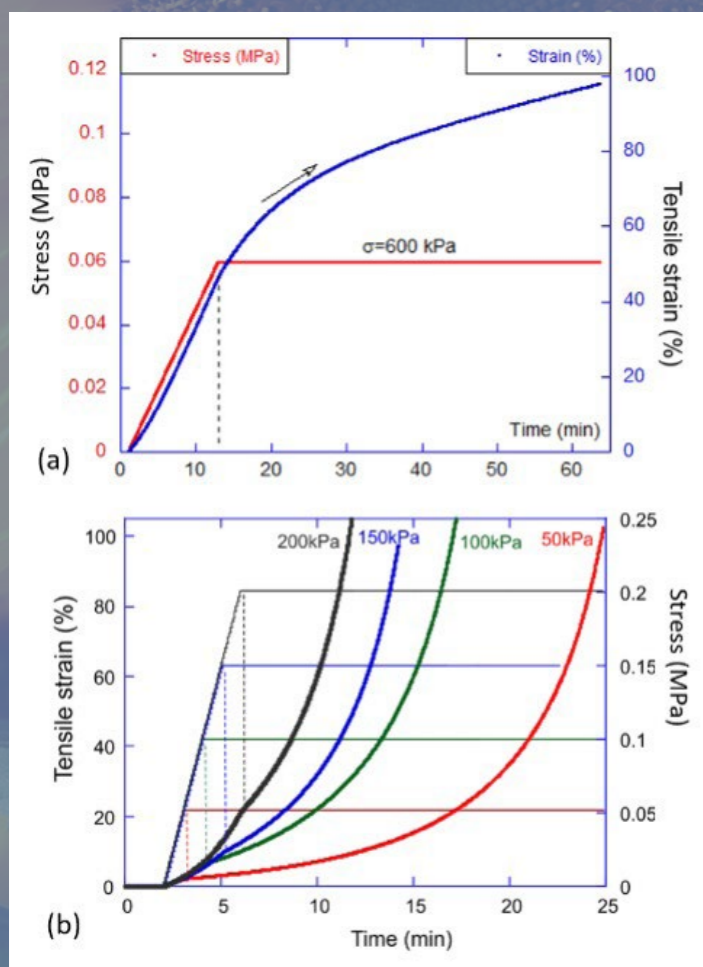


Figure 2: An illustration of plastic creep in xLCE. a) The plastic flow (creep) test: at a constant temperature (200°C), the tensile stress is ramped, and then kept constant. The strain continues to increase at a variable rate depending on the system. b) An illustration of the rate of non-linear plastic creep in xLCE depending on the level of constant stress. Such a test reveals the conditions and the time required to 'program' the uniaxial alignment in xLCE.

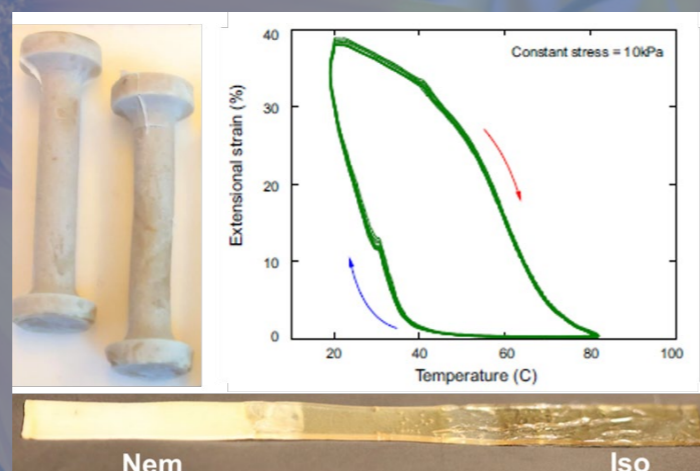


Figure 3: Actuator shape for linear contraction/extension, designed and moulded to reduce stress concentration points (leading to elastomer fracture). Ten repeated cycles of heating and cooling illustrating the reproducible actuation stroke of about 40%. At the bottom, a photo of an elastomer strip made by welding three different materials: left to right - nematic xLCE with high transition temperature, nematic xLCE with low transition temperature, and an isotropic exchangeable elastomer. Different parts of such a composite sample undergo actuation at different temperatures.

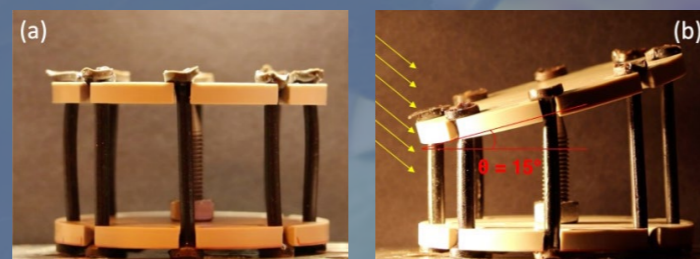


Figure 4: Heliotracking device, which tilts its top plate towards the Sun and tracks it as the light source rotates around it (like the face of sunflower). We think of an application of such a device as a platform for solar cells, maximising its useful flux during the daytime.

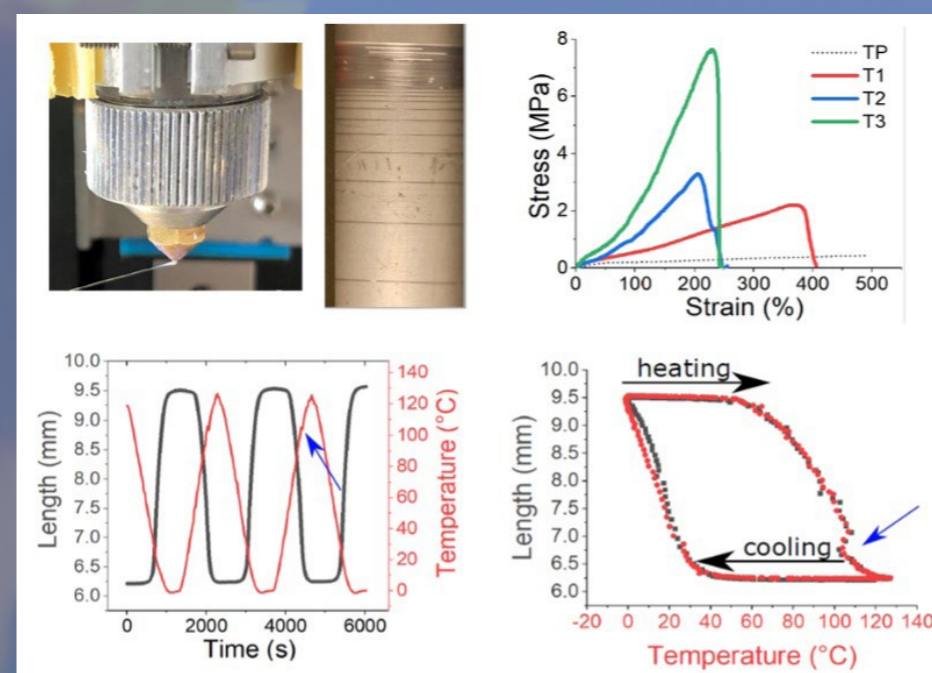


Figure 5: The 3D printer head and extruding xLCE fibre, collected on a bobbin. The stress-strain data shows high tensile strength of aligned fibres, which spontaneously change their length on repeated heating/cooling cycles

The exciting application of light-induced actuation is the heliotracking device shown in Figure 4. The other important direction of our work is in developing strong filaments and fibres of xLCEs, which would retain their thermal or photo-actuating characteristics while having tensile strength suitable for textile applications. Using the 3D printer extrusion head, we spin the textile grade xLCE fibres, their strength and reversible

actuation is illustrated in Figure 5.

In conclusion, the impetus of this APRA project continues to push boundaries of smart, functional materials that combine the active response to external stimuli with the full re-processability—the latter allowing the design of practically useful actuator shapes while maintaining a full range of recycling and re-programming options for these materials.

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PROJECT SUMMARY

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PROJECT LEAD

Eugene M. Terentjev is the Professor of Polymer Physics at the University of Cambridge, working in the Cavendish Laboratory since 1992. He obtained his MSc in Physics from Moscow State University in 1981 and PhD in 1985, before taking a postdoctoral position at Case Western Reserve University in 1990. He works on a broad range of topics, ranging from LCEs and dynamic polymer networks to molecular and cell biophysics, using both theoretical and experimental approaches.

PROJECT PARTNERS

The APRA project undertakes a lot of joint development with a technology startup company: Cambridge Smart Plastics Ltd.

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FUNDING

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme under grant agreement No.786659.