NEMATIC LIQUID CRYSTAL ELASTOMERS AS ARTIFICIAL MUSCLE MATERIALS

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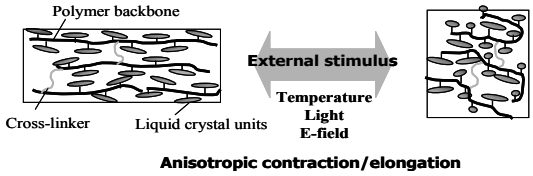
Abstract

Novel liquid crystalline elastomers with properties that mimic the action of a muscle have been developed. Uniaxial contraction of free standing film of the material can be achieved by heating the film through the nematic to isotropic phase transition. Thermoelastic response shows strain changes through the nematic –isotropic phase transition of about 30-35 %. Retractive force of nearly 450 kPa was measured in the isotropic phase. Static workloop studies show that the visco-elastic losses in these materials to be very small.

Introduction

There is increasing interest in the area of actuators in general [1-4] and artificial muscles in particular [5-7]. A wide range of materials have been tried including electrostrictive polymers [1], conducting polymers [2], hydrogels [3], and liquid crystal elastomers (LCEs)[4-6]. Supramolecular ordered assemblies such as liquid crystals provide an excellent framework for incorporating anisotropy as well as functionalities in materials that respond to external stimuli. Slight crosslinking of polymeric liquid crystals show elasticity similar to conventional elastomers. In such a crosslinked polymer, it is possible to create deformations on macroscopic length scales by changing the orientational order of the mesogenic group by external stimuli (Scheme 1). The uniqueness of the Liquid Crystalline Elastomer lies in its anisotropic response to external stimuli such as temperature[8], light [9] or electric field. In the nematic phase, the orientational order of the mesogen, forces the polymer backbone to be elongated along the average direction of orientation of the mesogens. However, upon heating into the isotropic phase, the nematic order is lost thereby allowing the polymer backbone to relax into its coiled conformation. LCEs provide a number of other advantages including the possibility of using them in the *dry* applications. Moreover, it is easy to introduce multifunctionality into them. LCEs by their very chemical nature have a number of *handles*, such as the liquid crystalline phase, density of crosslinking, flexibility of the polymer backbone, coupling between the backbone and liquid crystal group and coupling between the liquid crystal group and the external stimuli. All these handles can be easily tuned to optimize the mechanical properties. In general, the elastomers most frequently studied have been those based on side-chain liquid crystalline polymers rather than the main chain systems. The elastomer network consists of a liquid crystal mesogen attached to a polymer backbone through a spacer. The system is then cross-linked by a suitable cross-linker as seen in Scheme 1.



Scheme 1. Concept.of liquid crystal elastomer as artificial muscle.

Our main objective at the Naval Research Laboratory has been to develop LCEs and demonstrate that their elastic properties are comparable to muscles. We have prepared anisotropic nematic films [8] and fibers [10] and evaluated their mechanical properties. We have synthesized a number of liquid crystalline monomers exhibiting nematic phase and chosen the one with the lowest nematic-isotropic transition temperature as our model monomer. By varying the composition of the elastomer, crosslinking temperature, and crosslinking method, we can tune the operating temperature, strain and force generation. The rate at which a muscle can work is

limited by three variables, the strain through which it can shorten, the stress it can exert, and the contraction frequency. The values of these three variables for a skeletal muscle, on an average, are 25 percent, 450 kPa, and 5-10 Hz respectively. We have been able to achieve values close to and sometimes exceeding these numbers; Our LCEs have shown strain responses of 45 percent, stress of 300 kPa, and evaluated mechanical relaxation time scales that would make sub-second actuation achievable. Isostrain studies on these nonlinear elastomers show that restoring force far greater than the skeletal muscles can be developed in these actuators. Studies on viscoelastic losses and work performed by these artificial muscle materials have also been conducted.

Results and Discussion

The LC elastomer consists of two acrylate monomers and a cross-linker mixed in a specific mole ratio. Details of the synthesis and preparation of the films or fibers can be found elsewhere [8,10].

Thermoelastic measurements.

Thermoelastic studies performed on an elastomer film prepared from a mixture of two liquid crystal monomers with different mole ratio are shown in Figure 1. The measurements were done on heating the sample at 0.5 ^{o}C/min and applied stress of 20 kPa. The strain was measured as a function of temperature at constant applied stress over a temperature range covering the nematic to isotropic phase transition. Figure 1 shows that there is a relation ship between the temperature at which the contraction/extension occurs (N-I transition) and the % ratio of the monomers that constitute the elastomer. A decrease of the N-I transition is observed as the dilution of the homopolymer (100 % MAOC4) is increased.

Figure 2 shows measurements performed on a 50/50 MAOC4/MACC5 film on both heating and cooling cycles for 5 values of applied stress. The length of the elastomer remains constant well in the nematic phase and starts to slowly decrease as the isotropic phase is approached. At the nematic to isotropic phase transition, a sharp decrease in length of ~30 % is observed followed by a slow decrease into the isotropic phase. On cooling the process is reversed with a sharp increase in length on going from the isotropic to nematic phase.

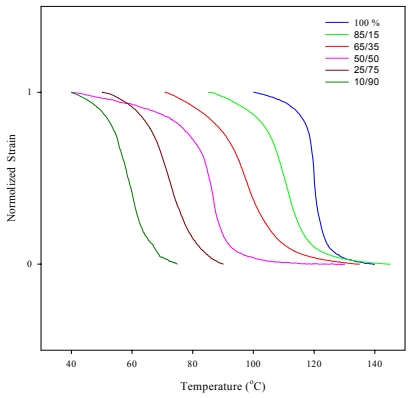


Figure 1. Transition temperature variation as a function of monomer ratio (MAOC4/MACC5).

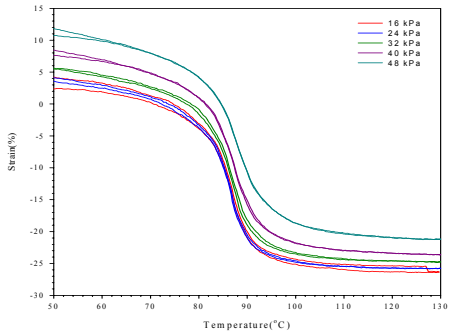


Figure 2. Thermoelastic measurements on a 50/50 MAOC4/MACC5 film at 0.5 ^{o}C heating and cooling cycles.

Isostrain measurements.

Stress vs strain plots were done at 60 ^{o}C, in the rubbery plateau region, at strain rate of 0.005 N/min, with a 4.5 kPa preload stress (Figure 3). The young's modulus was determined from the initial slope at small stress values and was found to be 4 MPa.

Long-term stability.

The LCE materials as free-standing films exhibit

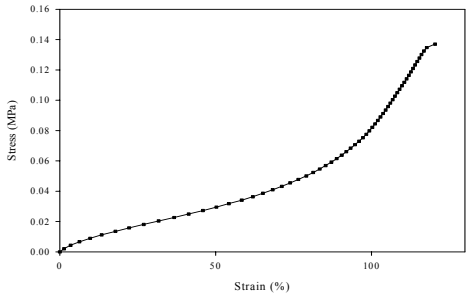


Figure 3. Stress-Strain Behavior of (50/50) MAOC4/MACC5 film with 5% cross-linking and a preload stress of 4.5 kPa.

actuation behavior in response to external stimuli, sustained over a long time period. Free-standing films were doped with a blue 633 nm diode dye and exposed to a laser beam. The heat generated by the absorption of the light by the dye is transmitted to the elastomer which contracts. The film showed an average 19% strain that remained unchanged over a period of 28 days. This time period corresponds to over 375,000 actuation cycles. The response time (both contraction and relaxation) depend on the ease and rapidity with which heat is conveyed to and from the bulk of the film via external sources/sinks.

Energy loss.

Passive work loops represent a measure of the inherent visco-elastic losses that the actuators must overcome in order to yield positive work output. The performance of any actuator would be diminished by large energy losses. Work loop experiments performed on our liquid crystal elastomer films showed very minimal energy loss compared to materials referred to in literature [11]. A static force was applied and the resulting clockwise work loops showed loss values between 0.07 J/Kg and 1.07 J/Kg. These loss values compared to the values reported (12 to 23 J/Kg) elsewhere [11], are very encouraging from the aspects of material and mechanical properties.

Work output.

For a biological muscle, the maximum work output ranges from 0.18 to 40.57 J/Kg [11]. Meijer and Full had established a protocol to measure the functional workspace of electroactive polymers (EAP) actuators using the same set up and techniques that they had used to test biological muscles. For their materials, the actuators had to be stimulated by an applied field in order to generate positive work. The resulting stress-strain plot will generate a counter- clockwise workloop, the amount of work generated being represented by the area within the loop. We used this general protocol to develop an active workloop for our materials in which the strain is induced by a temperature change. The workloop was generated using two isotonic cycles during which the temperature was stepped up or down at a fast rate while keeping the force on the muscle constant. These two isotonics were interspersed with two isothermal cycles in which the force was varied at a constant rate while holding the temperature either in the nematic or isotropic phase. The workloops thus obtained generate work outputs ranging from 4.8 J/Kg to 12.8 J/Kg. Increased crosslinker concentrations and multi-dentate crosslinkers are currently under investigation in order to increase the work output even closer to the maximum output of biological muscles.

Alternate actuation stimuli.

In addition to heat as external source of actuation stimuli, conducting polymer coatings have also been found viable. Coatings of the conducting polymer over free-standing LCE films, were found not to diminish mechanical properties while retaining continuity across the length of the film. Thermoelastic and stress-strain experiments were performed on these films. The strain at the nematic-isotrpic transition was roughly 19% for a coated film compared to 25% for an uncoated film. The resistance across the film before and after did not change indicating that the conducting polymer coating conformed to the LCE film during and after actuation ithout any breaks in the coating.

Conclusion.

We have shown that nematic elastomers can be drawn into well oriented films or fibers which can exhibit muscle-like physical properties with an elongation up to 35% and blocked stress of 450 kPa, numbers which are very similar to that exhibited by skeletal muscles. We have shown that the actuation can be accomplished both by temperature and light as stimuli. In our efforts to develop voltage responsive actuators from these liquid crystal elastomers, we have synthesized new materials with large permanent dipole moments. Efforts to develop a conformal conductive coating on such films are being pursued using conductive polymers. The visco-elastic losses in this elastomer

are very small suggesting that the material acts like a spring. The elastomer can be coated with conducting polymers without affecting the mechanical properties. Additional experiments with regard to active work-loops, stability and optimization of the modulus of elastomer have to be carried out in order to consider these materials as artificial muscle actuators.

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