Defence Research and Development Canada
Recherche et développement pour la défense Canada

CAN UNCLASSIFIED

DRDC | RDDC
technologysciencetechnologie

Auxetic materials

Project final report

Royale S. Underhill
DRDC – Atlantic Research Centre

Defence Research and Development Canada
Scientific Report
DRDC-RDDC-2017-R128
March 2018

CAN UNCLASSIFIED

Canada

IMPORTANT INFORMATIVE STATEMENTS

Endorsement statement: This publication has been peer-reviewed and published by the Editorial Office of Defence Research and Development Canada, an agency of the Department of National Defence of Canada. Inquiries can be sent to: Publications.DRDC-RDDC@drdc-rddc.gc.ca.

Abstract

The Canadian Army's Soldier System 2030 plan will take advantage of advancements in technologies and materials to provide the most effective equipment to the dismounted soldier. This includes lightweight armour with improved performance. It has been postulated in the literature that negative Poisson's ratio, auxetic materials may find application in an armour system, providing impact protection or behind armour blunt trauma mitigation. During the past four years, Defence Research and Development Canada (DRDC) has been exploring as a proof-of-concept, the physical properties of regular open cell polyurethane foams, compressed to form re-entrant structures. Finite element modelling of the foams has been performed to understand their response to compression. The project has also started to design various macromolecules as potential auxetic materials. This involved developing a multi-scale simulation for predicting physical properties, such as Poisson's ratio, of compounds. Two potentially auxetic compounds were synthesized: calixarenes and banana-phase liquid crystals. Unfortunately both compounds were insoluble, preventing them from being processed into a form to measure their physical properties.

Significance for defence and security

Lightweight armour systems are necessary in situations where there are weight restrictions such as personal protection, helicopters, patrol boats and transportable shelters. Negative Poisson's ratio (auxetic) materials have shown increased shear modulus, increased fracture toughness, and improved impact resistance. All properties beneficial for armour systems. This project focussed on the formulation of auxetic polymer foams and solid polymers. These materials may find applications for improved impact protection in items such as helmets, shin, elbow and knee pads. The auxetic foams may provide improved protection against behind armour blunt trauma.

This project started as a technology investment fund project, and was recognized as being high risk. After the restructuring of DRDC projects, it was recognized that the outputs of this project would benefit the Soldier System Effectiveness project and was incorporated there.

Résumé

Le plan du système du soldat de l'Armée canadienne de 2030 tirera profit des avancées dans les technologies et le domaine des matériaux afin de fournir l'équipement le plus efficace au soldat débarqué, notamment en lui offrant un blindage léger plus performant. Dans la littérature, on affirme que des matériaux auxétiques à coefficient de Poisson négatif pourraient être utilisés dans les systèmes de blindage. En effet, ils offriraient une protection contre les chocs ou atténueraient les effets d'un traumatisme contondant derrière le blindage. Depuis quatre ans, Recherche et développement pour la défense Canada explore, à des fins de validation de principe, les propriétés physiques de mousses de polyuréthane classiques à alvéoles ouvertes qu'on comprime pour qu'elles forment des structures réentrantes. Pour mieux comprendre comment les mousses réagissaient à la compression, on les a soumises à une modélisation par éléments finis. Dans le cadre du projet, on a aussi entrepris la conception de diverses macromolécules comme matériaux auxétiques potentiels. Pour ce faire, on a élaboré une simulation multiéchelle afin de pouvoir prédire les propriétés physiques des composés, comme le coefficient de Poisson. Deux composés auxétiques potentiels ont été synthétisés : les calixarènes et les cristaux liquides en phase banane. Malheureusement, ces deux composés sont insolubles, ce qui empêche de leur donner une forme permettant d'en mesurer les propriétés physiques.

Importance pour la défense et la sécurité

Les systèmes de blindage léger sont nécessaires dans les situations où le poids doit être limité, par exemple pour la protection individuelle, à bord d'hélicoptères ou de navires-patrouilleurs et dans la fabrication d'abris portatifs. Les matériaux (auxétiques) à coefficient de Poisson négatif ont démontré un accroissement du module de cisaillement et de la tenacité, ainsi qu'une meilleure résistance aux chocs. Toutes ces propriétés sont à l'avantage des systèmes de blindage. Ce projet a surtout porté sur la formulation de mousses de polymères auxétiques et de polymères solides. Ces matériaux pourraient servir à améliorer les casques de protection contre les chocs, les protège-tibias, protège-coudes et protège-genoux par exemple. Les mousses auxétiques pourraient offrir une meilleure protection contre les traumatismes contondants derrière le blindage.

Ce projet a été lancé dans le cadre du Fonds d'investissement technologique et on l'a reconnu comme présentant un risque élevé. Après la restructuration des projets de Recherche et développement pour la défense Canada, on a reconnu que les résultats de ce projet pouvaient profiter au projet sur l'Efficacité du système du soldat (ESSdt) et on l'a donc intégré à ce titre.

Table of contents

List of figures

List of tables

1 Introduction

The realities of modern combat demand lightweight armour with improved performance. While being lightweight, armour systems need to have toughness and strength. It has been postulated that negative Poisson's ratio, auxetic materials may be used in armour systems, providing impact protection or behind armour blunt trauma mitigation, while not contributing to excessive weight [1]. Such properties can lend themselves to a wide range of applications such as helmets, bullet proof vests [2], shin pads, elbow pads and knee pads [3]. Helmets, elbow and knee pads may also benefit from another property of auxetic materials, synclastic curvature. That is, they bend in the same direction in both perpendicular planes, producing a dome which doesn't have folds or seams (Figure 1). A lack of seams or joints provides for a structure that may have improved failure mechanisms.

Isotropic auxetic materials contract in the directions orthogonal to a compressive load (Figure 2). When the material contracts, it becomes more dense, increasing indentation resistance (H) [4]. The indentation resistance is proportional to the square of the Poisson's ratio (ν) as given by equation 1, so as the ratio approaches the limit of -1, the indentation resistance increases greatly. Negative Poisson's ratio foams may be of use in armour systems. Foams are typically too soft for structural applications, but may lend themselves to armour padding, in order to reduce behind-armour blunt trauma (BABT).

$$H \propto (1 - \nu^2)^{-x} \tag{1}$$

While near-zero and negative Poisson's ratio materials exist in nature, they are few. To date most manufactured auxetic materials have been foams or woven structures, that is, the negative Poisson's ratio was engineered into the macroscopic structure. Auxetic behaviour is not scale-dependant and can be approached at three levels. The first (macroscale level) is to engineer re-entrant structures into the architecture of the system. The second (mesoscopic level) is to design a material such that it has a re-entrant cellular structure (e.g. foam) or a fibril/nodule structure (e.g. polymer powder processing). The final (molecular level) is to design the material to have an inherently auxetic molecular structure. The advantage of a material where the auxetic property is inherent in the molecule or its interchain packing distance is that it would not be limited by production processes, and would find broader applications.

There have been a few different approaches to designing molecular auxetic materials. Simulations have shown negative Poisson's ratio in highly repetitive molecular networks with bonds emulating a re-entrant structure. These structures would be extremely challenging to synthesize due to their order, and rigid bond structures.

This project didn't look at the engineering of structures to form macroscale auxetics. Rather, it focussed on (1) creating re-entrant foams (mesoscale) and (2) designing and synthesizing molecules to exhibit negative Poisson's ratio (molecular scale). This project started as a

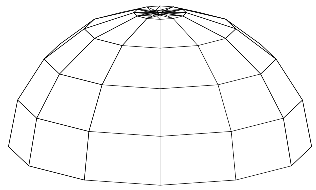


Figure 1: *Example of synclastic curvature for planar auxetic materials.*

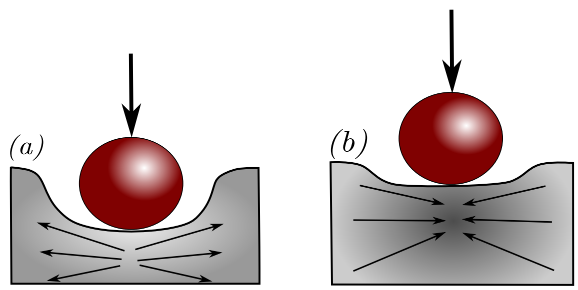
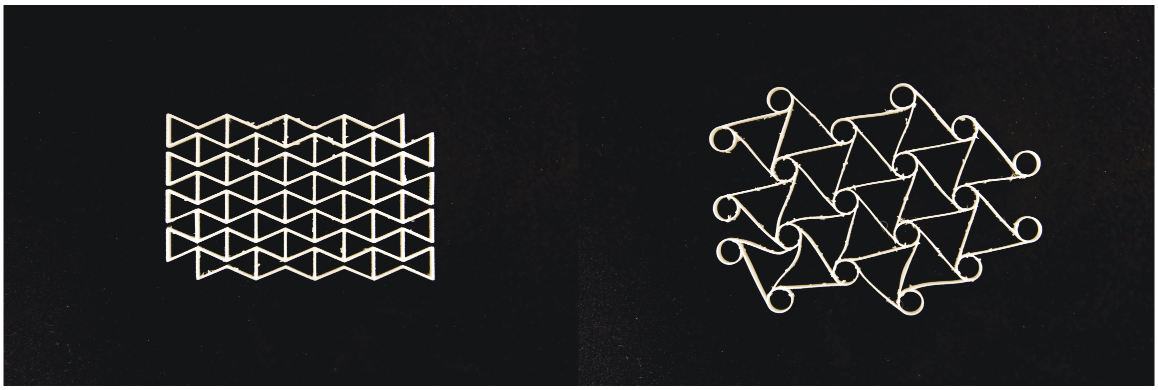


Figure 2: *Illustration of the response of (a) positive Poisson's ratio material, (b) negative Poisson's ratio material to compression in the y-direction.*

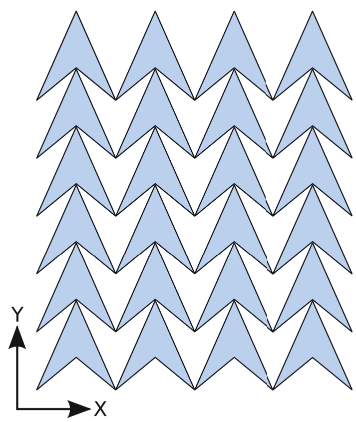
technology investment fund project, and was recognized as being high risk. After the restructuring of DRDC projects, it was recognized that the outputs of this project would benefit the Soldier System Effectiveness project and was incorporated there.

2 Mesoscale

The term re-entrant is defined as an angle pointing inwards [5]. When used with respect to auxetic materials, it refers to the angles of the ribs in a unit cell of the structure. There are a number of idealized re-entrant cellular structures that yield negative Poisson's ratios. Figure 3 shows a re-entrant bowtie (3a) and a chiral structure (3b), both were 3D printed in-house and exhibit 2D negative Poisson's ratio (in the xy-plane). Figure 3c also shows another re-entrant structure, the double arrowhead. The work reported here used the re-entrant bowtie structure as the idealized cell for modelling.



(a) *Bowtie.* ***(b)*** *Chiral.*



(c) *Double arrowhead.*

Figure 3: *Idealized 2D re-entrant cell structures.*

2.1 Production and characterization of auxetic foams

In this project foams represent the mesoscopic scale. Polymeric foams with negative Poisson's ratios are formed by tri-axially compressing regular foams. The compression deforms the polyhedron cells into a collapsed re-entrant structure (Figure 4). These compressed foams are then heat annealed, and cooled to lock-in the new cellular structure [6].

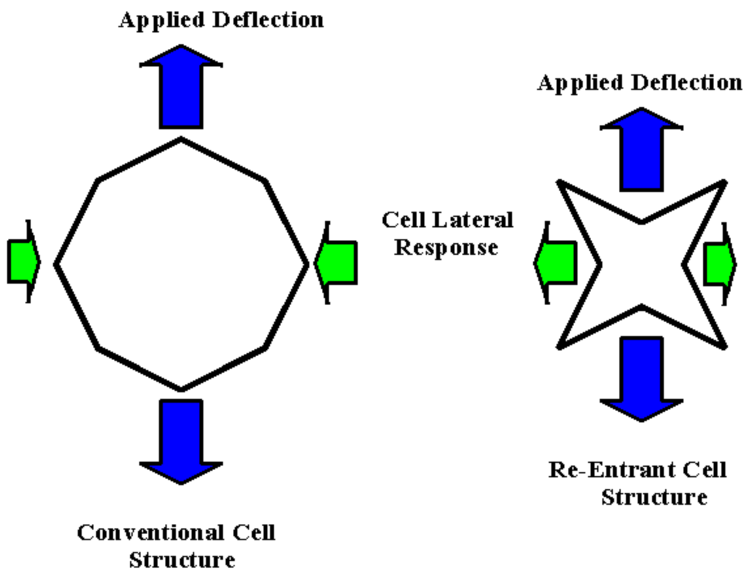
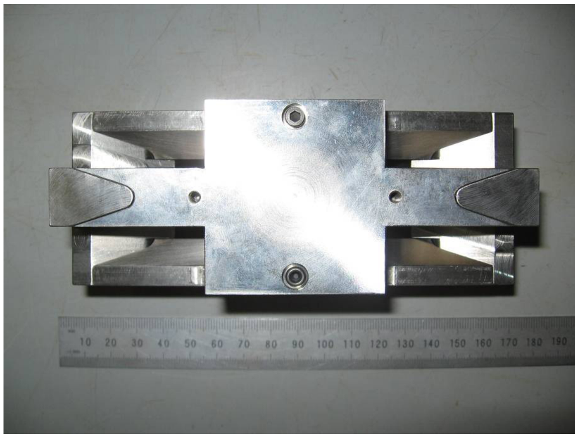


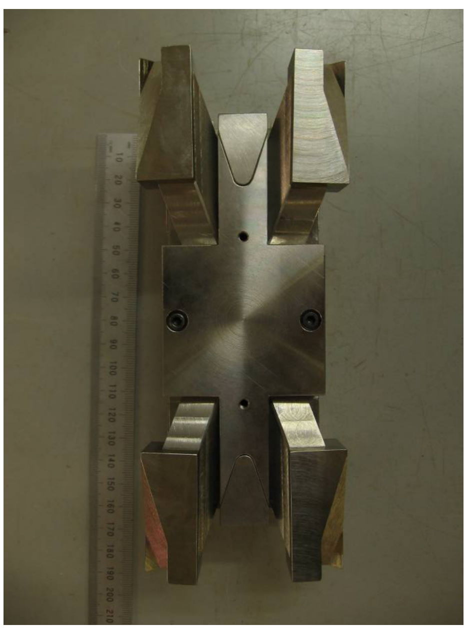
Figure 4: *Schematic of how compression deforms a foam cell into a re-entrant structure.*

Previous work reported in the literature creating polymeric auxetic foams used moulds of fixed shape, usually a segment of tube [6,7]. The methodology involved two-steps to achieve tri-axial compression. A non-processed foam sample of predetermined dimensions would be inserted into the tube mould, compressing in two dimensions. Plungers applied the pressure resulting in compression in the third, longitudinal dimension. Previous work reported in the literature technique results in wrinkles and buckling of the foam. Under contract to DRDC – Atlantic Research Centre, FACTS Engineering was able to create a mould that achieves uniform, simultaneous, triaxial compression with minimal buckling [8]. The basic design utilized a novel compression mould (Figure 5) which applied uniform strain to the six sides of a rectangular foam coupon simultaneously. The efficacy of the apparatus to form re-entrant cellular structures in foam was verified by optical microscopy (Figure 6).



(a) *Static frame.*

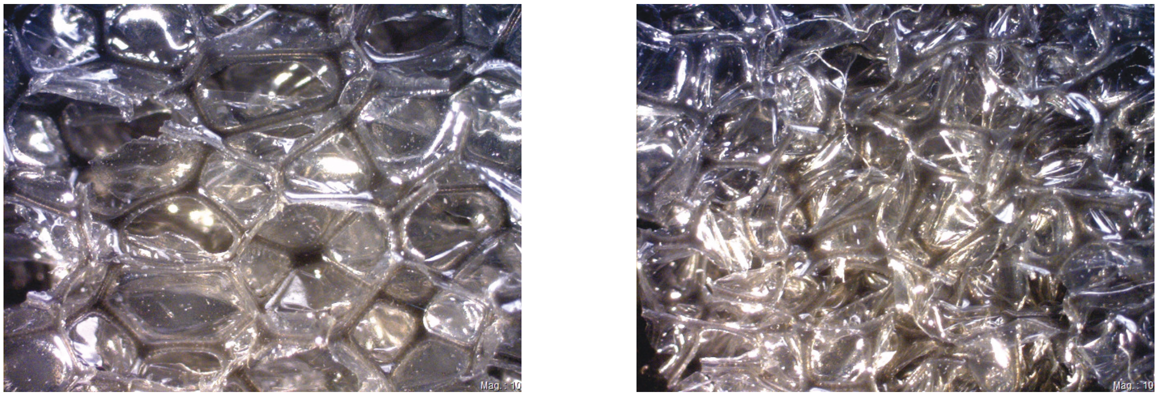
(b) *Movable corner.*



(c) *Fully assembled mould.*

(d) *Load frame.*

Figure 5: *Triaxial compression apparatus components.*



(a) Before. *(b)* After.

Figure 6: *Image of cell structure of 30 pores per inch polyurethane foam before and after triaxial compression, compression factor = 2.7.*

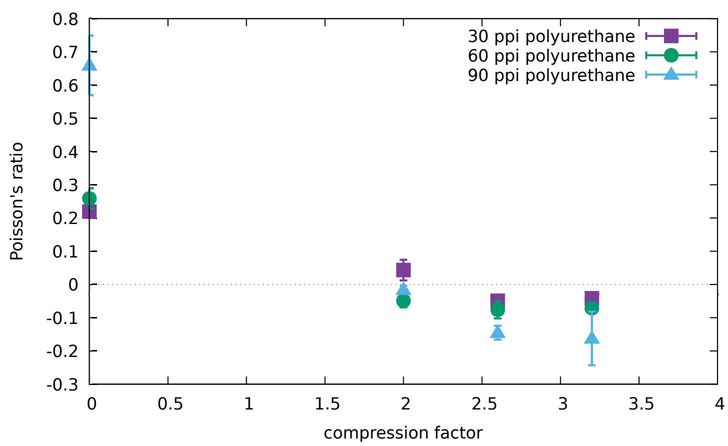


Figure 7: *Poisson's ratio as calculated using optical comparitor for 30 PPI, 60 PPI and 90 PPI polyurethane open cell foams.*

This novel mould was used to explore the compression of polyurethane foams. Three foams, of differing pore sizes (30, 60 and 90 pores per inch (PPI)), were compressed by three different amounts (compression factors of 2.0, 2.7 and 3.2). The Poisson's ratio of the resulting specimens was measured using an optical comparator. The results are given in Figure 7. All three foams successfully yielded negative Poisson's ratio materials. All the foams had a Poisson's ratio approaching or crossing zero at a compression factor of 2.0. The smallest pore size (90 PPI) gave the lowest Poisson's ratio (-0.16), at a compression factor of 3.2. this is in the range reported in the literature for polyurethane auxetic foams, which are listed as $-0.22 < \nu < -0.04$ [9].

The novelty of the foam work was in the creation of a compression mould that compressed triaxially, simultaneously. The ability to create foams with negative Poisson's ratio has been transitioned to Natural Resources Canada, Canmet Energy. They are exploring novel materials as backing personnel armour, as part of a project with DRDC – Valcartier Research Centre.

2.2 Modelling impact properties of auxetic foams

Some of the improved properties of auxetic materials are predicted by theory and some have been demonstrated in experimental studies. Often, too many variables are changed at once, making it difficult to determine if the change in performance can be attributed to the re-entrant geometry. Other variables that may be important for foams, but are regularily ignored include: areal density, void fraction, exact cell geometries, and impact conditions. This work examined the behaviour of idealized auxetic foams subjected to impact loads. The objectives of this study were to develop and test a finite element (FE) modelling methodology, examine the effect of void fraction and cell geometry on impact behaviour, examine the full compression of auxetic foam as well as the partial compression with a planar impacter and with a cylindrical impacter. All resting on a rigid surface. This work was carried out by Martec Limited under contract to DRDC – Atlantic Research Centre [10,11].

Foams with both conventional (hexagonal) cells as well as auxetic (re-entrant bowtie) cells

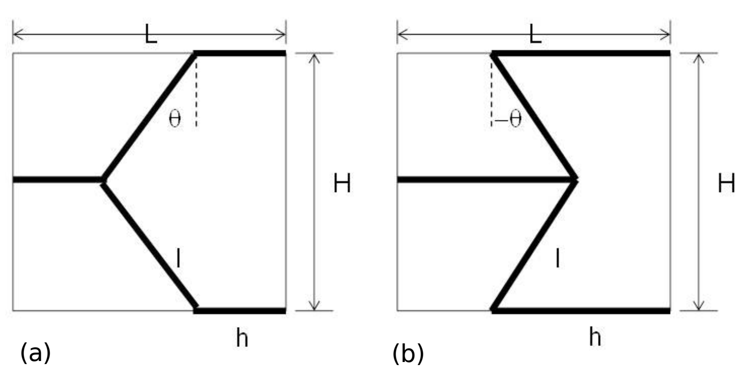


Figure 8: *Finite Element cells for (a) conventional and (b) re-entrant foams.*

were modelled. Figure 8 shows the unit cell where L=H=1.0 mm. The models used the quasi-static and stress relaxation properties of polyurea. In previous numerical studies of polymeric coatings the non-linear viscoelastic material model in LS-DYNA was used. However, it resulted in numerical errors when used with the shell elements in this study, so a piecewise linear elastic-plastic constitutive model was used. This material model allows the user to explicitly specify stress-plastic strain curves at each strain rate value.

The impact of a rigid plate or cylinder with a foam material resting on a frictionless rigid surface was studied. The initial FE model development and testing looked at small deformations with linear static analysis (Table 1). Analytical solutions were obtained using equations derived by Gibson [12] and Masters [13], where Gibson et al. [12] assumed that the deformations in the cellular structure were dominated by flexing of the cell walls, whereas Masters and Evans [13] took into account the more complex combination of flexure, stretching and hinging deformations. The work of Gibson et al. [12] dealt solely with honeycomb structures and was able to validate their model against experimental values, whereas Masters and Evans [13] compared honeycomb with re-entrant structures. Since 2D re-entrant structures were not available, Masters and Evans were not able to validate their model against experimental data.

In order to achieve LS-DYNA and VAST predictions that agreed with the analytical solutions, the following conditions were implemented. The specific LS-DYNA contact option was required for the contact algorithm, otherwise greater than 100% compaction was achieved. The model used hourglass modes with 3D solid elements. Friction was required between ribs. The FE model was 16 or 32 unit cells wide. The model was tested with and without x-constraints, and both explicit and implicit FE algorithms showed good results.

Once the FE model was developed and confirmed accurate, a parametric study was performed under large deformations, see Table 2. Rib angle, void fraction, and direction of impact (x-direction vs. y-direction) were explored. The areal density was maintained at approximately 2.64 g/cm^3 for all cases by varying the number of unit cells along with the void fractions. For small strains, the analytical and FE models gave similar results, both predicting auxetic behaviour for re-entrant geometry foams. For large strain, dynamic behaviour, the response is complex. The re-entrant geometry clearly exhibits auxetic behaviour, however the peak impacter force depends on void fraction, rib angle, and cell orientation (vertical or horizontal unit cell orientation). The parametric study showed that similar to conventional foams, the impact force has two distinct phases in mechanical response to impact load. At the beginning it has a very low resistance to the impacter, which is dominated by the bending deformation of the cell ribs. In the second phase, the stiffness increases rapidly due to the material becoming more compact. When all the voids are eliminated, the material acts as a solid polymer. The parametric study using the solid substrate showed that the impacter force and the force transmitted to the substrate were of the same magnitude.

The numerical techniques used to verify the model indicated that the rubber-to-rubber friction between the deformed ribs of the re-entrant cell has a significant influence on the

Table 1: *Initial development/ testing of FE models.*

Foam Type	Angle	Method	ν_{zx}	ν_{xz}	E_z(MPa)	E_x(MPa)
Conventional	20	Gibson*	1.374	0.728	1.316	0.697
		Masters*	1.151	0.659	1.057	0.606
		VAST	1.162	0.690	1.149	0.632
		LS-DYNA	1.200	0.690	1.210	0.640
Re-entrant	-20	Gibson*	-1.374	-0.728	0.773	0.410
		Masters*	-1.208	-0.662	0.660	0.362
		VAST	-1.216	-0.657	0.713	0.361
		LS-DYNA	-1.220	-0.687	0.721	0.376

* analytical results for small deformations [12, 13].

Table 2: *Parametric study parameters.*

Compression Type	Impacter	Backing
full	planer	none
> full	planer	none
partial	planer	none
partial	cylinder (5 mm)	none
partial	cylinder (5 mm)	solid substrate

predicted mechanical behaviour of the auxetic material. All parametric studies indicated that the geometric angle of the ribs was inversely proportional to the resistance to the impacter at the beginning of the transient. Also, for a set void fraction and geometric angle, the conventional materials showed more resistance to the impacter than the re-entrant materials. The re-entrant structures had a nearly elastic response to the high local strain rates, indicating that the samples almost always recovered fully after the impacter was removed.

Although the FE modelling showed no clear benefits using re-entrant structures over regular cellular foams, it should be noted that the re-entrant structures were idealized and 2-dimensional. True auxetic foam cells are less like the bowtie structure as seen in Figure 6. Actual experimental testing of auxetic foam is required to confirm or refute the simulation results.

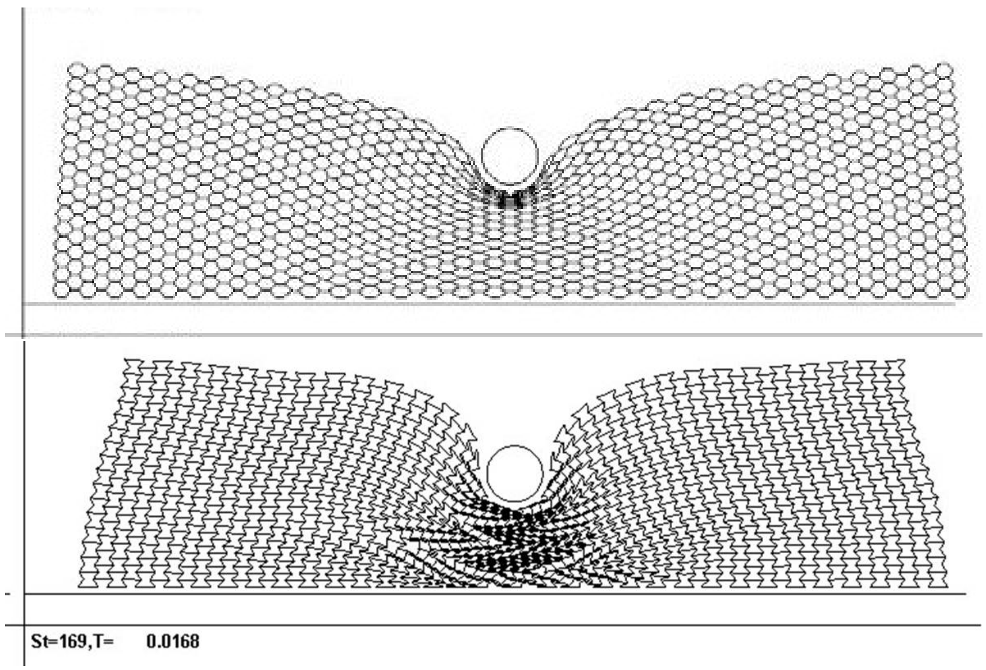


Figure 9: *FE simulation of partial compression with a cylindrical impacter. Top: standard honeycomb. Bottom: re-entrant structures.*

3 Molecular scale

Auxetic properties are not scale dependant, and as such it is believed that a compound could be synthesized that has a similar re-entrant structure on the molecular scale to that which has been modelled on the mesoscale. Although rare, these structures exist in nature, e.g., crystalline structures such as α-cristobalite [14] and zeolites [15, 16]. A number of hypothetical molecular auxetic compounds have been proposed in the literature, such as 1-4-reflexyne [17] and polytriangles-2-yne [18], which draw on the re-entrant structures such as are shown in Figure 3. Unfortunately, due to the high symmetry and multiple triple bonds, these molecules are impossible to synthesize. It was the goal of this research to investigate macromolecular compounds that were realistic to synthesize, and had near-zero or negative Poisson's ratio.

3.1 Multiscale simulation

Synthesizing compounds in the hopes of stumbling onto one that has bulk properties with negative Poisson's ratio is a laborious and expensive venture. It makes much more sense to model such compounds in order to predict potential condidates prior to synthesis. The first simulation of auxetic compounds was carried out in 1987 [19], however to date, no inherently auxetic materials on a molecular scale have been realized.

Multiscale simulation spans a number of length scales, from quantum mechanical to atomistic to coarse-grained to mesoscale. The goal of multiscale simulation is to calculate material properties on one level using models from different levels. Multiscale simulation is the key to achieving precise and accurate predictive tools for material properties. As an illustration of its importance; the development of a multiscale model using both classical and quantum mechanical theory to model complex chemical systems was the topic of the 2013 Nobel Prize in Chemistry [20–22].

The work reported here developed a strategy to predict the Poisson's ratio of known amorphous polymers [23]. The simulation strategy was developed and tested under contract by Dr. Armand Soldera of the Université de Sherbrooke. Using polymers where the experimental data was known allowed for the validation of the simulation. The simulation starts with optimizing the molecular structure using classical energetic criteria. Then both the thermal and mechanical equilibria are determined. Thermal equilibrium was achieved via a simulated heating/cooling process, whereby the minimum energy was determined. Normally this is where simulations move on to molecular dynamics, but Soldera postulated that reaching a mechanical equilibrium was mandatory to compute mechanical properties (i.e. Poisson's ratio) [23]. This was achieved by iteratively compressing the edges of the simulation cell and recording the potential energy. The results yield a minimum energy with respect to the cell volume which corresponds to the mechanical equilibrium.

Two common polymers were chosed to validate the multiscale simulation approach. They were poly(methyl methacrylate) (PMMA) and poly (tetraethylene glycol methacrylate)

(PTGM). These polymers were chosen because their experimentally determined Poisson's ratios approach zero. Mechanical properties were calculated before and again after the mechanical equilibrium step. It was seen that the systems resulting from just a thermal equilibrium did not provide realistic properties, where as once the system was brought to mechanical equilibrium, the mechanical properties were more in line with the experimental data reported in the literature (Table 3) [24].

In order to adopt the simulation strategy for potentially auxetic compounds, it was necessary to adapt it to obtain mechanical equilibrium for anisotropic materials. Classic anisotropic materials that already have experimental data are liquid crystals, so these were studied first to validate the adaptations. The difference when working with anisotropic molecules is that the order by which the optimization in the three directions (e.g., x, y, z) occurs, matters. For example x, y, z gives different configurations and energies to y,x,z. Fortunately these initial dissimilarites, when operated on via molecular dynamic simulations yield mechanical properties that are essentially the same.

From here, it was possible to extend the simulation strategy to re-entrant honeycomb structures such as Grima et al's 1-4-reflexyne [17] (Figure 10) and Wei's double arrow honeycomb [25] (Figure 11) already explored in the literature, validating the strategy against the simulation data in the literature. Table 4 shows the mechanical properties before and after the mechanical equilibrium step. Both the reflexyne and double arrow structures yielded negative Poisson's ratios after the mechanical equilibrium step.

It was shown that the addition of a compression/expansion element to determine mechanical equilibrium provided a vital step in the simulation of the mechanical properties of amorphous as well as anisotropic compounds. To our knoweledge, this is the first time that mechanical equilibrium has been incorporated into the molecular simulation of auxetic compounds. This strategy can be used to screen compounds based on their Poisson's ratio prior to lengthy and difficult syntheses. Dr. Soldera has extended the use of mechanical equilibrium to examine other properties such as glass transition temperatures of polymers.

Table 3: *Computed and experimental mechanical properties for PMMA and PTGM.*

Polymer		Before Mechanical Eq	After Mechanical Eq	Experimental [24]
PMMA	E(GPa)	10±5	4.4±1.0	2-3
	G(GPa)	50±66	1.6±0.4	1-2
	ν	0.4±0.4	0.31±0.08	0.3-0.4
PTGM	E(GPa)	5.4	6.4±1.1	n/a
	G(GPa)	2.3	2.2±0.4	n/a
	ν	0.33	0.34±0.11	0.2-0.5

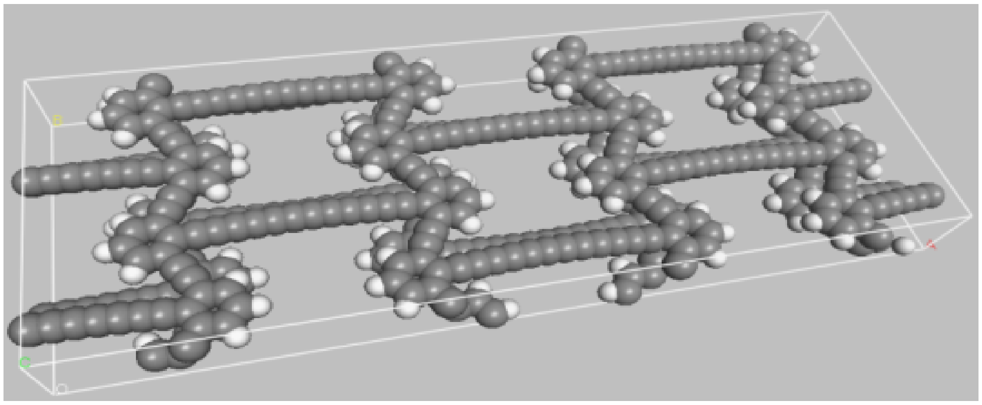


Figure 10: *Simulation of 1-4-reflexyne.*

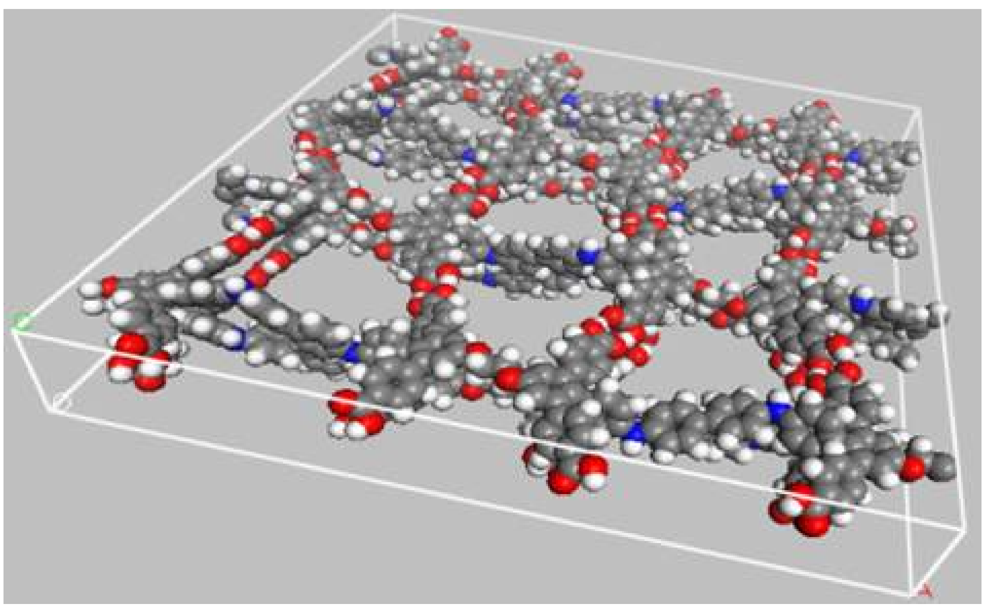


Figure 11: *Simulation of double arrow honeycomb.*

Table 4: *Computed and literature mechanical properties for reflexyne and double arrow structures.*

Polymer		Before Mechanical Eq	After Mechanical Eq	Literature
reflexyne [17]	E_x(GPa)	81	90±2	114.28
	E_y(GPa)	81	52±1	78.40
	G_{xy}(GPa)	3.4	0.5±0.1	2.75
	ν_{xy}	-0.22	-0.82±0.02	-0.46
	ν_{yx}	-0.19	-0.47±0.01	-0.31
double arrow [25]	E_x(GPa)	21.0±0.1	7.2±2.0	18.41
	E_y(GPa)	8.5±0.1	14.0±3.0	26.78
	G_{xy}(GPa)	0.08±0.11	0.28±0.14	n/a
	ν_{xy}	0.12±0.05	-0.15±0.08	-0.23
	ν_{yx}	0.05±0.01	-0.25±0.05	-0.34

3.2 Synthesis

For polymers to exhibit auxetic behavior in all three dimensions, a 3-dimensional cross-linked network is essential, but at the same time extensive cross-linking typically results in lower solubility and processability. Therefore, to design functional auxetic polymers it is essential to control the delicate balance between reticulation and mechanical properties. For reticulation, "nodes" can be incorporated to act as pivot points. Calixarene- and resorcinarene-derivatives have flexible bowl shapes. Other interesting molecular structures with potential auxetic properties were liquid crystalline polymers such as those proposed by Griffin et al [26–28]. The liquid crystal structures investigated by Griffin et al. did not exhibit negative Poisson's ratios, however there is a new class of liquid crystals to explore, banana phase liquid crystals.

3.2.1 Calixarenes

Grima et al. [29] hypothesized that calixarene-based polymers would exhibit negative Poisson's ratios because the bucket-like structure can open/close like an umbrella (see Figure 12). Calixarenes are macrocycles of four phenyl groups joined with ethyl linkages. Under contract, Dr. Olivier Lebel at the Royal Military College of Canada (RMCC) synthesized three calixarene structures as shown in Figure 13 [30], based on published synthetic methods. The products were verified at each stage using H-NMR (proton nuclear magnetic resonance spectroscopy). The lower rim of the calixarenes had four functions groups, all methoxyl terminated. The concept was that the methoxyl groups would be used to create anchoring points for short chain polymers such as polyurethanes. Thus the calixarenes were the nodes that provided auxetic movement as well as crosslinking to a polymer.

The calixarenes were supplied to DRDC – Atlantic Research Centre, where their physical properties were evaluated. The calixarenes, as provided by RMCC were less than 0.5 mg quantities. They were all white or off-white powders. They were analysed by dynamic scanning calorimetry (DSC), and the glass transitions temperatures (T_g) for all three calixarenes were found to be $\sim$70°C. Because all the samples were powders, they needed to be fabricated into a form that could be tested mechanically. Initial plans were to polymerize the calixarenes with polyurethanes, but this would require the powders to be soluble. They were found to be primarily insoluble in common polar and nonpolar organic solvents. Of the solvents explored, dimethylsulfoxide (DMSO) and dimethylformamide (DMF) were the most promissing, with the calixarenes being partially soluble. However, when the solvent was driven off, the resulting samples were not robust, and broke apart under minimal manipulation. This was due to the molecules being too short to intertwine (i.e. too low molecular weight). Essentially, once the solvent evaporated, there were no polymer chains to hold the structure. Pellets formed by compression did not have enough coherence to withstand mechanical testing, and the quantities of materials were too small for melt moulding/extrusion. At this point the calixarenes were abandonned due to problems with processing.

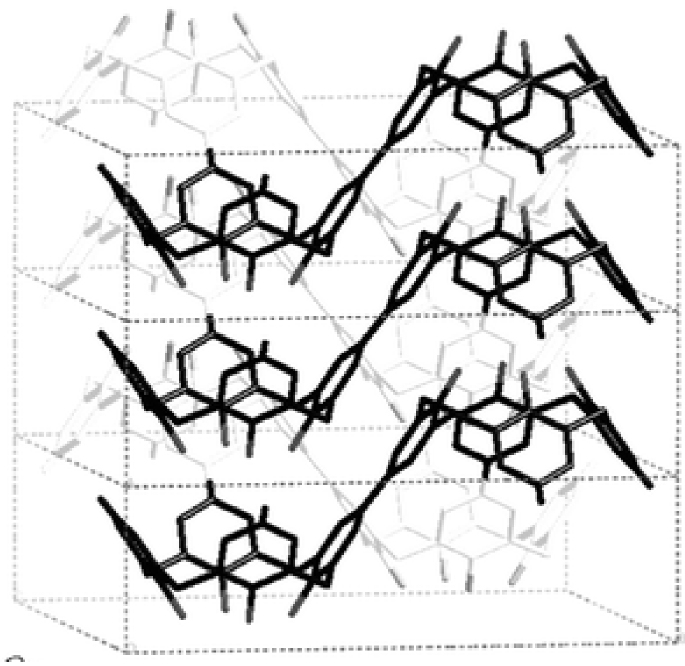
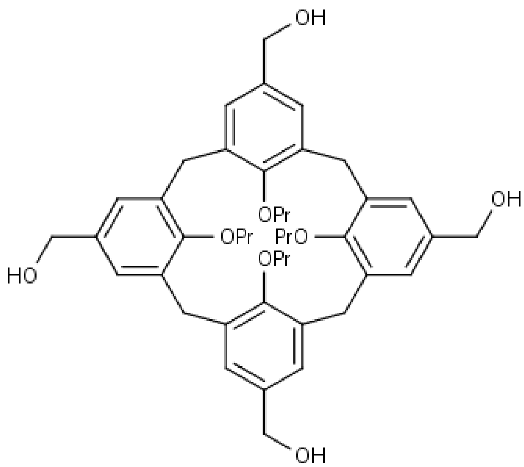
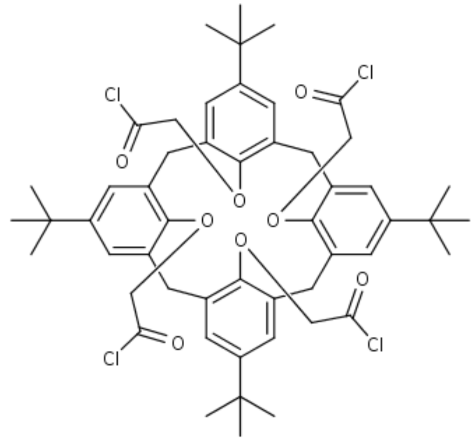


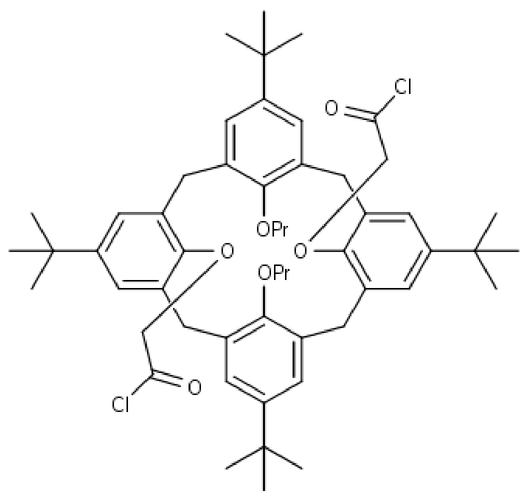
Figure 12: *3D molecular structure of calixarene macromolecules. Three units stacked.*



(a) Methoxyl/propoxy terminated.



(b) t-butyl/acid chloride terminated.



(c) t-butyl/mixed propoxy/acid chloride terminated.

Figure 13: *2D molecular structures of synthesized calixarenes.*

3.2.2 Banana-phase liquid crystals

Banana-phase liquid crystal (BPLC) polymers are polymers with non-chiral, bent mesogens. They are a relatively new field of liquid crystals [31, 32]. It is believed that in a relaxed state, the mesogens organize in a smectic phase, and when under tension they misalign, forming a B-phase which causes them to expand (Figure 14). Based on this hypothesis, and multiscale simulation of liquid crystal polymers [23], the banana-phase liquid crystal mesogen in Figure 15 was synthesized by RMCC. Six compounds were synthesized with this mesogen as the base. All were polymers where the number of methyl groups between each mesogen was varied from four to 12. The products were verified by Fourier transform infra-red spectroscopy (FTIR).

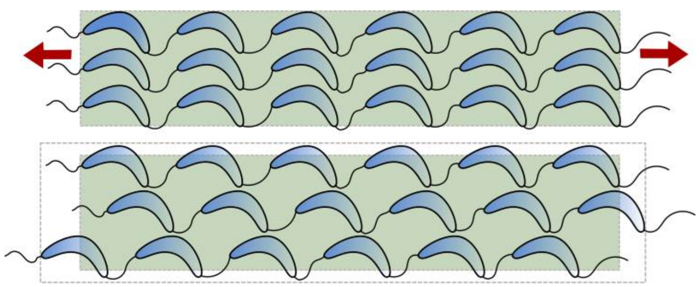


Figure 14: *Banana-phase Liquid Crystals relaxed and under tension, showing possible auxetic motion.*

The BPLC were supplied to DRDC – Atlantic Research Centre, where their physical properties were evaluated. The BPLC, as provided, were all white, off-white, or light yellow powders. They were analysed using DSC and were found to melt at $\tilde{2}$00–210°C. The Dockyard Laboratory Atlantic reconfirmed the structures of the samples using FTIR (Figure 16).

Again the polymers provided needed to be fabricated into a form that could be tested mechanically. The material was not soluble in mild solvents (i.e. DMF or DMSO). Fritsch and Merlo have observed strong pi-stacking in crystal phases of other BPLC systems [33], thus it is believed that the pi-conjugation in the mesogen leads to long range intermolecular interaction in our system, resulting in low solubility. When more aggressive solvents were used the BPLC decomposed. The BPLC mesogen contains imine linkages (i.e. C=N) known as Schiff bases. Fritsch and Merlo outline the inherent chemical, thermal and photo-physical instability of Schiff bases [33]. These functionalities are susceptible to hydrolysis in acidic environments with very low moisture content. The degradation of the Schiff base linkage in the BPLC results in the whole molecule falling apart. Further exploration of the literature

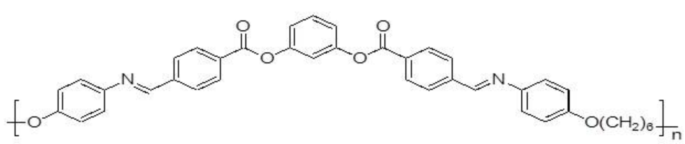


Figure 15: *Molecular structure of banana-phase liquid crystal mesogen.*

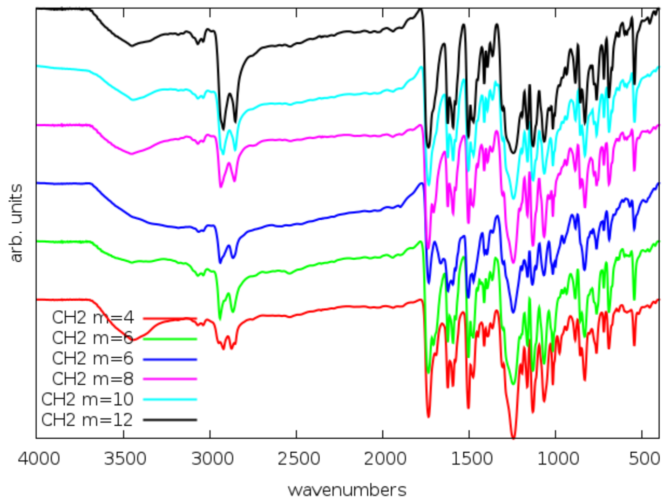


Figure 16: *FTIR spectra of Banana-phase Liquid Crystal polymers.*

showed that if a tertiary-butyl group was added in the ortho position to the Schiff base, then the BPLC structure showed better solubility in mild solvents [34]. Unfortunately, the project had reached the end, and no more time or money was allocated to explore alternative BPLC molecular structures.

4 Conclusions

A novel mould that achieves uniform, simultaneous, triaxial compression with minimal buckling was designed, built and tested. Polyurethane foams compressed in this mould to a minimum compression factor of 2.0 where shown to have negative Poisson's ratios. This mould is an improvement over the method reported in the literature which uses a two-stage tube and plunger system which can result in wrinkles and buckling. Despite efforts to improve precision for the measurement of Poisson's ratio, it was found that visual inspection in the form of a optical comparitor was the most best technique, yielding both accurate and precise results.

FE modelling of re-entrant honeycomb structures showed no clear benefits over regular hexagonal cellular foams in the mitigation of impact (i.e. compression). However, the re-entrant structures were idealized and 2-dimensional. True auxetic foam cells are more complex shapes, as seen in Figure 6. Actual experimental testing of auxetic foam is required to confirm or refute the simulation results.

Reaching a mechanical equilibrium prior to performing molecular dynamics simulation in amorphous systems leads to an accurate prediction of mechanical properties. A novel a multiscale simulation procedure was developed that can be used to systematically compare performance of potential auxetic materials. To our knowledge, this is the first of it's kind.

Two types of molecules were synthesized: calixarenes and banana-phase liquid crystals. The chemical structures were all verified by H-NMR and FTIR. Although the building blocks were successfully created, a problem with solubility was encountered. The production of molecular-scale auxetic materials was the riskiest part of this project. To the best of my knowledge, since their discovery in 1987, no materials have been synthesized and shown to exhibit negative Poisson's ratios based on their molecular structure. It is unfortunate that this project did not surpass this hurdle.

5 Future work

There is currently a project at DRDC – Valcartier Research Centre on lightweight materials to mitigate behind armour blunt trauma. Part of this project is looking into novel materials, including auxetic materials. To support this new work, and to find an exploitation route for auxetic foams, the triaxial compression apparatus has been loaned to Natural Resources Canada, Canmet Energy. They are the lab testing armour with different backing materials for DRDC – Valcartier Research Centre.

The use of auxetic foams as liners for athletic equipment is being explored by Alderson at Bolton University in the U.K. [35,36]. As this is related to the use of auxetic foams in soldier personal protective equipment, a tech watch on Alderson's research should be maintained.

Banana-phase liquid crystal polymers may still show auxetic properties. New synthetic routes that either stabilize the Schiff base, or use another chemical group could be explored.

6 Reports and presentations

- KarisAllen, K. (2013), Development of Equipment for the Manufacture of Auxetic Foam for DRDC, (DRDC Atlantic CR2013-042) FACTS Engineering Inc.
- Jiang, L., Pearson, D., MacKay, K. (2013), Modeling of Impact Properties of Auxetic Materials — Phase 1, (DRDC Atlantic CR2013-103) Martec Ltd.
- Jiang, L., Pearson, D., Dunbar, T. (2014), Modeling of Impact Properties of Auxetic Materials — Phase 2, (DRDC-RDDC-2014-C174) Martec Ltd.
- Underhill, R. (2014), Defense Applications of Auxetic Materials, *DSIAC Journal*, 1, 7–13.
- Al Hujran, T. Lebel, O. (2014), Synthesis and Characterization of Polycalix[n]-arenes, (DRDC-RDDC-2014-C013) Royal Military College of Canada.
- Porzio, F. Soldera, A. (2015), Molecular Simulation of Molecular Auxetic Building-blocks — Final Report, (DRDC-RDDC-2015-C222) Universit/'e de Sherbrooke.
- Underhill, R., Soldera, A., Lebel, O. (2015), Auxetic Materials — From Theory to Reality. Invited speaker at IRM Research Day. Abstract and 20 slides.
- Underhill, R., Lebel, O., Soldera, A. (2015), Exploring Novel Polymers and Foams as Possible Auxetic Materials. Poster at 98th Canadian Chemistry Conference and Exhibition. Ottawa, ON.
- Underhill, R., Lebel, O., Soldera, A. (2015), Exploiting Auxetic Behaviour in the Search for New Armour Materials. Invited speaker at Auxetics 2015. Abstract and 25 slides.
- Jokar, M. Lebel, O. (2016), Synthesis of Banana-Phase Mesogens for Potential Auxetic Materials — Final Report, (DRDC-RDDC-2016-C028) Royal Military College of Canada.
- Porzio, F., Cuierrier, E., Wespiser, C., Underhill, R., Soldera, A. (2016), Molecular Simulation as a Guide for Potential Auxetic Materials. Invited speaker at Auxetics 2016. Abstract and 50 slides.
- Porzio, F., Cuierrier, E., Wespiser, C., Underhill, R., Soldera, A. (2017), Mechanical Equilibrium, a Prerequisite to Unveil Auxetic Properties in Molecular Compounds, *Molecular Simulation*, 43, 169–175.
- Soldera, A., Porzio, F., Cuierrier, E., Wespiser, C., Underhill, R. (2017), Can We Design Auxetic Polymers at a Molecular Level? Speaker at the 9th International Convference on Materials for Advanced Technologies. Abstract. DRDC-RDDC-2017-R17-0608-1236.
- Underhill, R. S. (2017), Manufacture and Characterization of Auxetic Foams, (R17-0525-0906) DRDC – Atlantic Research Centre. submitted for document review

References

[1] Liu, Q. (2006), Literature Review: Materials with Negative Poisson's Ratios and Potential Applications to Aerospace and Defence, (Technical Report AR-013-0622) Defence Science and Technology Organization.

[2] Baughman, R. H. (2003), Avoiding the shrink, *Nature*, 425, 667.

[3] Yang, W., Li, Z.-M., Shi, W., Xie, B.-H., and Yang, M.-B. (2004), Review on auxetic materials, *Journal of Materials Science*, 39, 3269–3279.

[4] Alderson, K. L. and Evans, K. E. (2000), The strain dependent indentation resilience of auxetic microporous polyethylene, *Journal of Materials Science*, 35, 4039–4047.

[5] (2017), Collins Dictionary (online), HarperCollins Publishers, www.collinsdictionary.com (Access Date: 2017-05-23).

[6] Lakes, R. S. (1987), Foam structures with a negative Poisson's ratio, *Science*, 235, 1038–1040.

[7] Chan, N. and Evans, K. (1997), Fabrication Methods for Auxetic Foams, *Journal of Materials Science*, 32, 5945–5953.

[8] KarisAllen, K. (2013), Development of Equipment for the Manufacture of Auxetic Foam for DRDC, (DRDC – Atlantic Research Centre CR2013-042) FACTS Engineering Inc.

[9] Scarpa, F., Giacomin, J., Bezazi, A., and Bullough, W. (2006), Dynamic behavior and damping capacity of auxetic foam pads, In *Proc–Spie Int Soc Opt Eng*, Vol. 6169, p. 61690T.

[10] Jiang, L., Pearson, D., and MacKay, K. (2013), Modeling of Impact Properties of Auxetic Materials – Phase 1, (DRDC – Atlantic Research Centre CR2013-103) Martec Ltd.

[11] Jiang, L., Pearson, D., and Dunbar, T. (2014), Modeling of Impact Properties of Auxetic Materials – Phase 2, Defence Research and Development Canada, (DRDC-RDDC-2014-C174) Martec Ltd.

[12] Gibson, L., Ashby, M., Schajer, G., and Robertson, C. (1982), The mechanics of two-dimensional cellular materials, *Proceedings of the Royal Society of London*, A382, 25.

[13] Masters, I. and Evans, K. (1996), Models for the elastic deformation of honeycombs, *Composite Structures*, 35, 403–422.

[14] Yeganeh-Haeri, A., Weidner, D. J., and Parise, J. B. (1992), Elasticity of α-Cristobalite: A Silicon Dioxide with a Negative Poisson's Ratio, *Science*, 257(5070), 650–652.

[15] Grima, J. N., Jackson, R., Alderson, A., and Evans, K. E. (2000), Do Zeolites Have Negative Poisson's Ratios?, *Advanced Materials*, 12(24), 1912–1918.

[16] Siddorn, M., Coudert, F.-X., Evans, K. E., and Marmier, A. (2015), A systematic typology for negative Poisson's ratio materials and the prediction of complete auxeticity in pure silica zeolite JST, *Phys. Chem. Chem. Phys.*, 17, 17927–17933.

[17] Evans, K. E., Nkansah, M., Hutchinson, I., and Rogers, S. (1991), Molecular network design, *Nature*, 353, 124.

[18] Grima, J. N. and Evans, K. E. (2000), Self expanding molecular networks, *Chemical Communications*, pp. 1531–1532.

[19] Wojciechowski, K. (1987), Constant thermodynamic tension Monte Carlo studies of elastic properties of a two-dimensional system of hard cyclic hexamers, *Molecular Physics*, 61(5), 1247–1258.

[20] Karplus, M. (2014), Development of Multiscale Models for Complex Chemical Systems: From H+H2 to Biomolecules (Nobel Lecture), *Angewandte Chemie International Edition*, 53(38), 9992–10005.

[21] Levitt, M. (2014), Birth and Future of Multiscale Modeling for Macromolecular Systems (Nobel Lecture), *Angewandte Chemie International Edition*, 53(38), 10006–10018.

[22] Warshel, A. (2014), Multiscale Modeling of Biological Functions: From Enzymes to Molecular Machines (Nobel Lecture), *Angewandte Chemie International Edition*, 53(38), 10020–10031.

[23] Porzio, F., Cuierrier, E., Wespiser, C., Underhill, R., and Soldera, A. (2017), Mechanical Equilibrium, a Prerequisite to Unveil Auxetic Properties in Molecular Compounds, *Molecular Simulation*, 43, 169–175.

[24] (2014), The Champman & Hall/CRC Polymers: A Properties Database (online), Taylor & Francis Group, www.polymersdatabase.com (Access Date: 2016-06-01).

[25] Wei, G. (2005), Design of auxetic polymer self-assemblies, *physica status solidi (b)*, 242(3), 742–748.

[26] He, C., Liu, P., and Griffin, A. C. (1998), Toward Negative Poisson Ratio Polymers through Molecular Design, *Macromolecules*, 31, 3145–3147.

[27] He, C., Liu, P., Griffin, A. C., Smith, C. W., and Evans, K. E. (2005), Morphology and Deformation Behaviour of a Liquid Crystalline Polymer Containing Laterally Attached Pentaphenyl Rods, *Macromolecular Chemistry and Physics*, 206, 233–239.

[28] He, C., Liu, P., McMullan, P. J., and Griffin, A. C. (2005), Toward molecular auxetics: Main chain liquid crystalline polymers consisting of laterally attached para-quaterphenyls, *Physica Status Solidi (B)*, 242(3), 576–584.

[29] Grima, J. N., Williams, J. J., and Evans, K. E. (2005), Networked calix[4]arene polymers with unusual mechanical properties, *Chemical Communications*, pp. 4065–4067.

[30] Al Hujran, T. and Lebel, O. (2014), Synthesis and Characterization of Polycalix[n]arenes, Defence Research and Development Canada (DRDC-RDDC-2014-C013) Royal Military College of Canada.

[31] Niori, T., Sekine, T., Watanabe, J., Furukawa, T., and Takezoe, H. (1996), Distinct ferroelectric smectic liquid crystals consisting of banana shaped achiral molecules, *J. Mater. Chem.*, 6, 1231–1233.

[32] Reddy, R. A. and Tschierske, C. (2006), Bent-core liquid crystals: polar order, superstructural chirality and spontaneous desymmetrisation in soft matter systems, *J. Mater. Chem.*, 16, 907–961.

[33] Fritsch, L. and Merlo, A. A. (2016), An old dog with new tricks: Schiff bases for liquid crystals materials based on isoxazolines and isoxazoles., *ChemistrySelect*, 1(1), 23–30.

[34] Erkenez, T. and Tümer, M. (2015), Polymer-anchoring Schiff base ligands and their metal complexes: Investigation of their electrochemical, photoluminescence, thermal and catalytic properties, *Arabian Journal of Chemistry*, pp. –. published online 9 May 2015.

[35] Sanami, M., Ravirala, N., Alderson, K., and Alderson, A. (2014), Auxetic materials for sports applications, *Procedia Engineering*, 72, 453–458.

[36] Allen, T., Martinello, N., Zampieri, D., Hewage, T., Senior, T., Foster, L., and Alderson, A. (2015), Auxetic materials for sports safety applications, *Procedia Engineering*, 112, 104–109.

DOCUMENT CONTROL DATA

*Security markings for the title, authors, abstract and keywords must be entered when the document is sensitive

1. ORIGINATOR (Name and address of the organization preparing the document. A DRDC Centre sponsoring a contractor's report, or a tasking agency, is entered in Section 8.) DRDC – Atlantic Research Centre PO Box 1012, Dartmouth NS B2Y 3Z7, Canada	2a. SECURITY MARKING (Overall security marking of the document, including supplemental markings if applicable.) CAN UNCLASSIFIED 2b. CONTROLLED GOODS NON-CONTROLLED GOODS DMC A

3. TITLE (The document title and sub-title as indicated on the title page.)

Auxetic materials

4. AUTHORS (Last name, followed by initials – ranks, titles, etc. not to be used. Use semi-colon as delimiter)

Underhill, R. S.

5. DATE OF PUBLICATION (Month and year of publication of document.)	6a. NO. OF PAGES (Total pages, including Annexes, excluding DCD, covering and verso pages.)	6b. NO. OF REFS (Total cited in document.)
March 2018	25	36

7. DOCUMENT CATEGORY (e.g., Scientific Report, Contract Report, Scientific Letter)

Scientific Report

8. SPONSORING CENTRE (The name and address of the department project or laboratory sponsoring the research and development.)

DRDC – Atlantic Research Centre
PO Box 1012, Dartmouth NS B2Y 3Z7, Canada

9a. PROJECT OR GRANT NO. (If appropriate, the applicable research and development project or grant number under which the document was written. Please specify whether project or grant.)	9b. CONTRACT NO. (If appropriate, the applicable contract number under which the document was written.)
02ab	

10a. DRDC DOCUMENT NUMBER	10b. OTHER DOCUMENT NO(s). (Any other numbers which may be assigned this document either by the originator or by the sponsor.)
DRDC-RDDC-2017-R128	

11a. FUTURE DISTRIBUTION WITHIN CANADA (Approval for further dissemination of the document. Security classification must also be considered.)

Public release

11b. FUTURE DISTRIBUTION OUTSIDE CANADA (Approval for further dissemination of the document. Security classification must also be considered.)

Public release

12. KEYWORDS, DESCRIPTORS or IDENTIFIERS (Use semi-colon as a delimiter.)

auxetic; molecular simulation; negative Poisson's ratio; armour; personal protective equipment; PPE

13. ABSTRACT/RÉSUMÉ (When available in the document, the French version of the abstract must be included here.)

The Canadian Army's Soldier System 2030 plan will take advantage of advancements in technologies and materials to provide the most effective equipment to the dismounted soldier. This includes lightweight armour with improved performance. It has been postulated in the literature that negative Poisson's ratio, auxetic materials may find application in an armour system, providing impact protection or behind armour blunt trauma mitigation. During the past four years, Defence Research and Development Canada (DRDC) has been exploring as a proof-of-concept, the physical properties of regular open cell polyurethane foams, compressed to form re-entrant structures. Finite element modelling of the foams has been performed to understand their response to compression. The project has also started to design various macromolecules as potential auxetic materials. This involved developing a multi-scale simulation for predicting physical properties, such as Poisson's ratio, of compounds. Two potentially auxetic compounds were synthesized: calixarenes and banana-phase liquid crystals. Unfortunately both compounds were insoluble, preventing them from being processed into a form to measure their physical properties.

Le plan du système du soldat de l'Armée canadienne de 2030 tirera profit des avancées dans les technologies et le domaine des matériaux afin de fournir l'équipement le plus efficace au soldat débarqué, notamment en lui offrant un blindage léger plus performant. Dans la littérature, on affirme que des matériaux auxétiques à coefficient de Poisson négatif pourraient être utilisés dans les systèmes de blindage. En effet, ils offriraient une protection contre les chocs ou atténueraient les effets d'un traumatisme contondant derrière le blindage. Depuis quatre ans, Recherche et développement pour la défense Canada explore, à des fins de validation de principe, les propriétés physiques de mousses de polyuréthane classiques à alvéoles ouvertes qu'on comprime pour qu'elles forment des structures réentrantes. Pour mieux comprendre comment les mousses réagissaient à la compression, on les a soumises à une modélisation par éléments finis. Dans le cadre du projet, on a aussi entrepris la conception de diverses macromolécules comme matériaux auxétiques potentiels. Pour ce faire, on a élaboré une simulation multiéchelle afin de pouvoir prédire les propriétés physiques des composés, comme le coefficient de Poisson. Deux composés auxétiques potentiels ont été synthétisés : les calixarènes et les cristaux liquides en phase banane. Malheureusement, ces deux composés sont insolubles, ce qui empêche de leur donner une forme permettant d'en mesurer les propriétés physiques.