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Review

Review of Auxetic Materials for Sports Applications: Expanding Options in Comfort and Protection

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Abstract: Following high profile, life changing long term mental illnesses and fatalities in sports such as skiing, cricket and American football—sports injuries feature regularly in national and international news. A mismatch between equipment certification tests, user expectations and infield falls and collisions is thought to affect risk perception, increasing the prevalence and severity of injuries. Auxetic foams, structures and textiles have been suggested for application to sporting goods, particularly protective equipment, due to their unique form-fitting deformation and curvature, high energy absorption and high indentation resistance. The purpose of this critical review is to communicate how auxetics could be useful to sports equipment (with a focus on injury prevention), and clearly lay out the steps required to realise their expected benefits. Initial overviews of auxetic materials and sporting protective equipment are followed by a description of common auxetic materials and structures, and how to produce them in foams, textiles and Additively Manufactured structures. Beneficial characteristics, limitations and commercial prospects are discussed, leading to a consideration of possible further work required to realise potential uses (such as in personal protective equipment and highly conformable garments).

Keywords: injury; impact; indentation; comfort; protective equipment; negative Poisson's ratio; foam; textiles; Additive Manufacturing; finite element modelling; auxetic

1. Introduction

Auxetic materials have a negative Poisson's ratio (NPR) [1], meaning they expand laterally in one or more perpendicular direction/s when they are extended axially. Poisson's ratio (ν) is the negative of the ratio of lateral to axial strain (Figure 1). The potential application of foams, textiles and additively manufactured (AM) auxetic materials to sporting protective equipment (PE), as well as other forms of impact protection, has been discussed in articles with a focus on materials (e.g., [2–5]) and sport (e.g., [6–8]). Auxetic foam was the first man made auxetic material [9], and makes up a significant proportion of the scientific literature and therefore this review. Foam studies typically use relatively established fabrication methods for auxetic polyurethane (PU) foams, with tests often based upon those outlined in standards used to certify sports safety equipment (i.e., British Standards

Appl. Sci. 2018, 8, 941 2 of 33

Institution—BSI, International Organization for Standardization—ISO, American Society for Testing and Materials—ASTM). Idealised structures (e.g., those fabricated via AM) and textiles can be designed to have repeat patterns that provide NPR in either one or two planes [5].

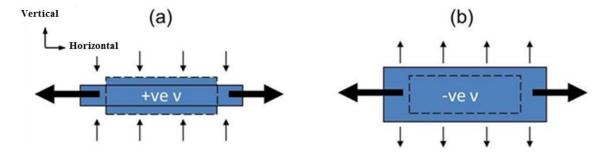


Figure 1. Lateral (vertical) deformation due to Poisson's ratio during tensile axial (horizontal) loading for (a) a conventional material and (b) an auxetic material. Thick and thin arrows correspond to deformation due to loading and Poisson's ratio respectively.

There are numerous reviews into auxetic materials and/or structures [10–17], but there has not yet been one focussing on their application to sporting goods. Deficiencies in standards (or a lack of a standard in some instances) and PE [18,19] indicate changes in equipment testing and design are likely, with the need for novel and improved materials to meet new requirements.

Recent developments in the fabrication of auxetic PU foam have deepened our understanding of the mechanisms that can fix an imposed cell structure, while improving and diversifying fabrication methods. Developments include rapid fabrications [20,21] and the ability to tailor elastic modulus and Poisson's ratios of anisotropic and gradient foam samples [22,23]. Finite element modelling (FEM) has been applied to auxetic materials [24–26] but has not been fully explored to support their implementation within sports equipment. With developments in AM [27], the creation of idealised auxetic structures (computationally tested using FEM) has become commercially viable [28]. Developing fabrication techniques for auxetic textiles and composites are also bringing both protective and form-fitting auxetic garments closer to realisation [29].

The focus of this review is on sports equipment and auxetic materials, predominantly auxetic foams, textiles and FEM/AM for impact protection. NPR can provide uniquely high indentation resistance [30,31] and fracture toughness [32], lending auxetic materials well to impact force or acceleration attenuating scenarios, regularly demonstrated by impacting auxetic foams [2,3,33]. Auxetics' multi-axial expansion [34,35] and double curvature [9,36,37] could improve comfort, fit and durability in sporting garments and personal protective equipment (PPE). Multi-axial expansion could also be useful in filtration applications [9,38–40], while gradient structures' enhanced bending stiffness [41,42] could reduce the mass of skis, snowboards, tennis rackets or hockey sticks (to name a few), without sacrificing stiffness. An initial summary of current sporting PE and PPE will lead to descriptions of common auxetic structures and materials, how to create them and how they could resolve issues in sporting PE, PPE, garments and other sports equipment.

2. Introduction to Sporting Protective Equipment

Injuries in sport are common and place a significant burden upon participants and national economies [43,44], estimated at \$525 (~£380) million per year in The Netherlands [45] for example. The main methods of intervention are elimination, modification (a reduction in severity or likelihood of injury) and reaction (i.e., medical) [44]. Preventative measures such as sports safety equipment, and/or rule changes, are more cost effective than reactive procedures [44] and successful products can increase a manufacturer's share of the sporting goods market (~\$90/£66 billion in the USA in 2017 [46]). Sporting PE is intended to reduce risks and is typically either an addition to the playing field or environment (i.e., crash matt or barrier, known herein as PE) or PPE. Both equipment

Appl. Sci. 2018, 8, 941 3 of 33

types provide; (i) protection against impact, dissipating and absorbing energy while reducing peak forces/accelerations, pressures and in some cases such as helmets, impulses [43,44,47–49] and (ii) protection from penetration, abrasions and lacerations [18,47,48,50]. Sporting PPE can also provide support to joints, muscles and the skeleton [18,44,47,48,51].

Sporting PPE (Figure 2a) often contains a shell—typically a stiff material or non-Newtonian fluid layer—to spread forces and reduce pressures [47,48,50,52]. Impacts are typically attenuated by elastic [44,52], viscoelastic and/or permanent deformation (i.e., crushable foam in cycling helmets) of a cushioning material with a lower compressive stiffness than the shell [47,48,50,52]. Visco-elastic and permanent deformation reduce impulses, improving the level of protection [44].

Sporting PPE must sometimes cover large areas and should ideally be low in mass and bulk to reduce restriction of movement, fatigue and heat build-up. Foam is typically used for the cushioning layer in PPE, and with limited thickness to compress and decelerate impacting bodies material selection is crucial. In contrast, PE such as crash mats (where bulk, mass and ergonomics are less critical) are often large and thick, allowing more gradual deceleration over a greater distance through compression of relatively compliant foam [52]. For both sporting PE and PPE, deceleration (or force) ideally reaches a maximum yet safe value at low strains, before plateauing and deforming with no additional load to safely maximise energy absorption (the integral of decelerating force with respect to deformation) before foam densification (at high strains) causes high deceleration (or force) [53]. Crash mats are used in a variety of conditions; protecting skiers, snowboarders and mountain bikers (who can travel at high speeds) from hazards on a mountain (i.e., lift poles or trees), often in extreme and variable climates, to providing padding to gymnasts on flat surfaces at room temperature.

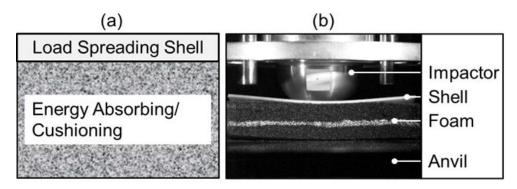


Figure 2. (a) Schematic of a typical piece of Personal Protective Equipment containing pressure dissipating material (hard outer shell) and energy absorbing/cushioning material (deformable foam); (b) Impact adapted from British Standard 6183-3:2000.

Sport safety equipment is often certified according to tests specified in standards and regulations (i.e., [54–58]), which typically specify a maximum allowable peak force/acceleration under impact (i.e., Figure 2b). To perform well in these tests, a product should absorb or dissipate as much energy as possible to prevent force/acceleration from passing its allowable limit [59]. Criteria within standards (such as impact energies, velocities and masses) are not always well justified and tests typically feature fixed rigid anvils rather than biofidelic (human like) surrogates, meaning they are not overly representative of the scenarios where the equipment may be required to perform [44]. In some cases there is no standard, so manufacturers certify products against a standard for another safety device, which can be misleading for consumers. McIntosh discusses the increased chance of injury when perceived protection offered by equipment is incorrect [19].

Crash mats are typically certified to BS EN 12503-1:2013 [60] as intended for gymnasium use, but include impact tests for outdoor activities such as pole vaulting. BS EN 12503-1:2013 is not reflective of the sometimes harsh and variable outdoor environment (weather conditions, surfaces, etc.) where these mats can be located, and tested parameters do not reflect realistic impacts [58]. There are

Appl. Sci. 2018, 8, 941 4 of 33

other occasions where specific standards are not available, and so a proxy is used. Two examples from snow sports are wrist protectors, certified to EN 14120:2003 [61] for roller sports [51], and back protectors, which are often certified to EN1621 (motorbike) [62]. Schmitt et al. found that snow sport participants expect back protectors to protect the spine, but EN1621 does not test against scenarios likely to cause spinal injury [18]. Inspection of PPE (impact shorts, knee guards, elbow guards and back protectors etc.) marketed for adventure sports including mountain biking, kayaking and snow sports shows EN1621 [62] & EN 14120:2003 [61] (for motor-biking) are repeatedly used in place of a dedicated standard.

Some standards have received criticism for not providing adequate tests even when applied to their intended field. Reaction to a number of high profile deaths and serious injuries as well as multiple awareness campaigns [63] raised the issue of helmet use in snow sports considerably, but head injury rates have remained fairly constant [63,64]. Scandals in the National Football League (NFL) culminated in high proportions of Chronic Traumatic Encephalopathy (CTE, up to 99% in a bias but large sample set) that could have contributed to early death, suicide and dementia in players [65].

In some cases, equipment and regulations intended to protect sports people are clearly unsatisfactory. As an example of equipment not meeting expectations, attenuation of rotational acceleration is thought to be critical in protection from concussion in sports [66,67]. Standards, however, typically assess helmets based upon their attenuation of linear accelerations (e.g., EN1077 & ASTM F2040, & F1446 [54,56,68]) and resistance to penetration (e.g., EN1077 [56]) based upon direct impacts [69,70]. Standards can be updated or replaced, for example BSI 6685-1985 for motorised vehicle helmets (a previous revision of Reference [71]) replaced BS2495:1977 and BS5361:1976 to include oblique impacts. The standard for cricket helmets (BS7928:1998) was amended (BS7928:2013) to include impacts by cricket balls [72] following findings that cricket helmets were not sufficiently attenuating acceleration under high speed impacts [73]. Commuter cycling (where cyclists travel alongside motor vehicles) is becoming increasingly popular due to clear benefits to health, congestion and emission levels, as well as improved facilities such as dedicated lanes. Safety concerns are a major barrier to participation in commuter cycling [74,75] but helmets are still only certified to protect from linear accelerations [76].

Sports equipment is a competitive, rapid uptake market. Manufacturers search for new technology to remain competitive, achieve the highest possible levels of certification and improve safety. One approach to solve the problem of rotational acceleration in helmets is a slip plane between the shell and crushable foam [77]. Slip plane technology is included in some commercial helmets, despite a lack of experimental evidence to support a reduction in concussion risk [78–81], highlighting the problem caused by insufficient standards. As an example of material development in sporting PPE, trends over the past twenty years have favoured lightweight, ergonomic equipment which does not sacrifice performance in standard tests [49]. Non-Newtonian fluids with high energy absorption were developed and can act as both a shell and cushion [82,83], offering comfort and flexibility under normal use and increased stiffness under impact. Non-Newtonian materials in isolation can pass certification tests for sporting PE and PPE [18,44,47,48,50]. Scientific literature highlights limitations in standards, as well as associated certified products including helmets [69,79–81], back protectors [18,50] and wrist protectors [51,84,85]. Recent trends look to include the use of more representative surrogates rather than rigid anvils [84,86,87] and tests designed for specific sports [50,51] to replace proxy standards (e.g., [61]). Solutions including novel materials are needed to reduce the effect of sports injuries and meet required improvements to standards (i.e., as per BSI 6685-1985 [71] and BS7928:2013 [72]).

3. Common Auxetic Materials and Structures

Auxetic research began in earnest with open cell foam [9], the first example of a man made NPR material. Subsequently, auxetic materials have now been developed or discovered in other nanocrystalline [88] and microporous [89]) polymer, ceramic [90], metallic [91] and composite [92] forms, and include natural systems [93]. Auxetic materials such as foams, textiles and AM structures

Appl. Sci. 2018, 8, 941 5 of 33

are often classed as mechanical metamaterials; with unexpected macro-scalar (effective) characteristics caused by their micro/nano-structure [15].

This section will first discuss the modelling of auxetic structures and mechanisms, before considering auxetic foam fabrication, properties and characteristics, followed by some of the other auxetic materials of relevance including textiles and those manufactured by AM.

3.1. Modelling Auxetic Materials and Structures

Numerical [94–97], molecular [98] and FE models [99–101] have all been applied to auxetic materials. These models, used individually or combined, typically analyse the elastic deformation mechanisms of auxetic materials. The most common microstructures of cellular auxetics can be designated into three types; re-entrant, chiral and rotating units (Figure 3a-c). The 2D re-entrant structure (such as Figure 3a,d) was the first to be modelled numerically [95] and was developed in early work on auxetic honeycombs and foams. Other early models included a mechanical model of isotropic 2D/3D frameworks of rods connected by sliding collars [102] and a thermodynamic model of a 2D assembly of hard cyclic hexamer 'molecules' [103]. Chiral auxetics (Figure 3b)—asymmetric structures that are non-superimposable on their mirror image [104]—achieve NPR through cooperative node rotation-induced bending of connecting ligaments. Rigid rotating units (Figure 3c) can have NPR, dependent on the rotation of connected squares [105] or other shapes [106–108], and this model has been used as an alternative to the re-entrant model in auxetic foams [109]. Other models and structures exist, including the missing rib model [110], cellular systems featuring pre-defined mechanical instabilities [111] and the nodule-fibril model for polymers [112]. Auxetic behaviour induced by elastic instability includes systems consisting of 2D tessellation of elliptical [113] and other shape [114,115] voids and 3D tessellations of holes [116]. Non-porous sheets with tessellations of spherical dimples have also been investigated for auxetic response [117].

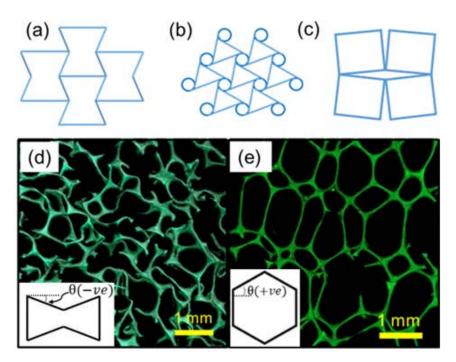


Figure 3. (a) Assembled 2D re-entrant structure; (b) 2D Chiral structure; (c) 2D rotating squares structure; (d) Micro Computed Tomography of polyurethane auxetic open cell foam (depth = 1 mm), pop-out showing simplified 2D diagram of a re-entrant cell, θ = re-entrant angle (negative value for angle below horizontal axes); (e) Micro CT scan of conventional open cell PU foam (depth = 1 mm), with pop-out showing simplified 2D diagram of a conventional polyhedral cell, θ = cell rib angle (positive value for angle above horizontal axes).

Appl. Sci. 2018, 8, 941 6 of 33

Re-entrant models have been used to investigate the deformation mechanics of cellular auxetics. Deformation due to flexure of the cell wall alone was initially considered, with the cell ribs assumed to behave as beams of uniform thickness [118]. Combined hinging (change of angle between ribs) and stretching (increase in rib length) of the cell wall was later modelled [98], as well as a 14-sided polyhedron, specifically for open cell foam, with cell rib bending as the main deformation mechanism [119]. All three deformation modes have been modelled simultaneously [96,120], confirming that the change of cell parameters (e.g., cell length or rib angle) directly affected Poisson's ratio and Young's modulus. The combined hinging, stretching and bending model [96] has been adapted to accurately predict the mechanical properties of gradient, isotropic and anisotropic auxetic foam [23].

Auxetic application in other fields has progressed with the use of FEM, such as auxetic cores used in sandwich plates that reduce shear stresses [121], anti-tetrachiral stents demonstrating desired radial expansion with axial stability [122] and smart auxetic honeycombs in structural health monitoring [123]. FEM can predict the effect of changing design parameters of auxetic structures, such as cell wall thickness [97,124], unit cell cross-sectional area [94], relative stiffness of modelled beams [125] and ratio of vertical to oblique cell wall length [126]. Simulation results could therefore aid and inform the design of future prototypes—e.g., to reduce a structure's mass while maintaining the maximum load it can support. FEM has also been used to develop understanding of the effect of plastic deformation on auxetic behaviour [127,128] and generate specific material models to explore impact resistance of auxetic honeycomb structures [129]. A framework for modelling auxetic foam using the continuum approach at large strains has been developed with FEM [130–132] and could be extended to model composite structures made from auxetic materials.

Several FEM studies established that the angle of re-entrant cell ribs effects Poisson's ratio [26,133–135], demonstrating cell parameter manipulation. FEM has also highlighted that other internal cell parameters (e.g., length, height, thickness) can be changed to tune the Poisson's ratio, and that flaws in the re-entrant cell structure can reduce NPR's magnitude towards zero [136]. Innovations are facilitated by FEM, such as the combination of two auxetic structures within one design (re-entrant hexagon and arrowhead) [137], honeycombs with ribs made of 2-phase composite material [138], the development of curved honeycomb unit cell designs [139], the creation of auxetic honeycombs inspired by the spider's web [140] and the formation of auxetic systems made out of readily available materials [141] and recycled rubber [142].

FEM has also been employed to model auxetic two-phase systems without voids by filling the spaces of a cellular first phase with a matrix second phase. This was an idea first postulated in 1992 and modelled analytically for elastically isotropic laminates by Milton [143] and using FEM for 'network embedded composites' by Evans and co-workers [144]. More recently, FEM has been extended to a two-phase core employing conventional and/or auxetic phases for out-of-plane auxetic behaviour [141], and to sandwich panel composites with the two-phase core employing established auxetic cellular structures and/or auxetic matrix [145–147], as well as structures developed using topology optimisation routines [145,148]. The ability to have temperature-dependent auxetic behaviour in such systems has also been investigated using FEM by allowing one or both phases to possess temperature varying Young's modulus [149,150].

The effect of design changes on Young's modulus and Poisson's ratio can be adjusted and improved before manufacture [121], and FEM can validate analytical results [151–158]. Full validation of FEM often requires comparison and agreement with experimental testing [159–167], which can potentially lead to extrapolation or tailoring of models for specific applications. Experimental test data can be input into FEM solvers to validate and develop material models [168]. With a validated model, design changes can be implemented and investigated without numerous iterations of manufacturing and testing. FEM can then be used alongside optimisation tools to further improve auxetic designs [169–173], although the 'modelling theory' remains to be examined stringently [174].

Appl. Sci. 2018, 8, 941 7 of 33

Dynamic effects can also be examined with explicit FEM solvers. The energy absorption of a re-entrant structure when crushed by a rigid wall has been analysed [175], but not experimentally validated. Analytical formulae were however used to validate FEM suggestions that auxetic honeycombs have higher energy absorption than conventional honeycombs in crushing strength analysis [176]. When varying the impact energy on a jounce bumper [27,177], FEM closely matched experimental values for the material's Poisson's ratio and compressive modulus and the jounce bumper's force and displacement. A subsequent auxetic bumper model showed less vibration in compression than a non-auxetic equivalent. A range of (FEM) parametric studies compared rate-dependent blast resistance performance in military applications [178,179]. Auxetic sandwich panels had higher impact resistance than their conventional counterparts, validated with comparison to analytical models rather than experimental data. Sporting PE and PPE typically aims to minimise harmful impact forces/accelerations through high strain rate compression of energy absorbing materials [180,181], and explicit solvers have previously facilitated such investigation [47,48,182].

3.2. Fabricating and Characterising Auxetic Foam

Auxetic foam is often fabricated to experimentally show expected enhancements (i.e., to impact force attenuation or vibration damping) due to NPR [2,3,33,183]. Auxetic foam fabrications typically change the cell structure of open cell foam (referred to herein as the parent foam) to give it an NPR. Lakes' thermo-mechanical fabrication method [9] first applies a volumetric compression ratio (VCR, normally defined as original/final volume and typically between 2 and 5 [184]) to a parent foam in all three orthogonal axes to buckle cell ribs [118]. The applied compression changes the cell shape and causes the re-entrant structure, as cell ribs buckle beyond \sim 5% compression [118]. The compressed foam is then heated to a set temperature to encourage permanent plastic deformation. The temperature is typically between 130 and 220 °C [13], often referred to as the 'softening temperature' [20,185]. Finally, the foam is cooled to fix the imposed structure [9]. Buckling the originally straight ribs (Figure 3e) gives the polyhedral cells a re-entrant, contorted cell structure [9] (Figure 3a,d). Typical sizes were initially small, in the order of $20 \times 20 \times 60$ mm (following fabrication), although larger 'scaled up' samples have subsequently been fabricated (e.g., [185–188]).

Fabrication methods for auxetic foams have developed and diversified since Lakes' initial study [9]. Stretching samples after cooling was introduced to reduce adhesion between cell ribs and residual stresses [189]. More recently, fabrication processes have been split into stages including; multiple heating cycles (with foam removed from the mould and stretched by hand in between to reduce residual stresses, flaws and creases [190]) and the addition of an annealing stage—heating below the softening temperature. Foams are typically annealed at 100 °C [37,185,190], but alternatives to annealing include slow cooling in the mould in air [20,191] or cooling outside the mould in air [192]. In an attempt to reduce creases and flaws when inserting foam into the mould, olive or vegetable oil and WD-40 have been used to lubricate moulds [185,189,193].

Another line of investigation has attempted to increase the range of Poisson's ratios and Young's moduli achievable following thermo-mechanical fabrications. The heat, time and compression applied during fabrication can be adjusted to give higher magnitude NPR and increased stiffness [129]. Heating for longer or at a higher temperature ('over-heating' while using typical compression levels) gives a positive or near zero Poisson's ratio re-entrant foam [30,194]. Over-heated re-entrant samples have comparable density to typical auxetic foams and a linear stress strain curve without the presence of a plateau region [30,194]. Comparing auxetic and over-heated foam with a positive Poisson's ratio [194] could demonstrate the effect of Poisson's ratio on characteristics such as vibration damping or impact force attenuation.

In depth analysis shows the complexity and diversity of chemical constitution in polymers (including those found in foams) [20]. Polymeric microstructure [20], and microstructural changes caused by heating [195] have only recently been investigated in relation to auxetic foam fabrication. Li & Zeng targeted styrene acrylonitrile copolymer (SAN) particle bonding, which has a glass transition

Appl. Sci. 2018, 8, 941 8 of 33

temperature of around $110~^{\circ}$ C. Such, or other, electron donating groups [15] can provide fixing mechanisms for imposed structures.

Sporting products often include foam sections which have a larger planar area than typical auxetic foam samples (\sim 20 \times 20 \times 60 mm) [9,185,196], and numerous scaled up fabrications have been attempted [4,7,23,185–187]. Large fabricated samples often exhibit random and ordered inhomogeneity. Random inhomogeneity is caused by flaws such as surface creasing [185], due to difficulty compressing large samples of foam into the mould [186]. Ordered inhomogeneity was observed in fabricated cubes (150 mm sides), where the centre had the lowest density [4,8]. Possible explanations include reduced compression towards the centre of the cube during fabrication or a thermal gradient that meant the internal structure was not sufficiently fixed and re-expanded following fabrication. The specific influence of temperature gradients and compression gradients during auxetic foam fabrication is unclear.

Solutions to increase homogeneity when fabricating large samples of foam include; (i) a mould with moveable walls which can be assembled around the foam and then used to apply compression [186,197]; (ii) a multi-stage compression process with an intermediate VCR to reduce insertion forces [185] and (iii) a vacuum bag to apply compression [187]. Vacuum bags can apply consistent pressure through thickness, reducing external densification and allowing fabrication of additional shapes (i.e., curved) [187]. Recent work utilising rods passing through large sheets of foam [7,8,23,188] is the only published method which seeks to apply controlled distribution of material within the mould. 'Felted foams' are fabricated commercially by compressing open cell foam between two heated plates to impart an anisotropic, re-entrant cell structure and direction dependent NPR [33].

Small scale fabrication parameters depend on the type of foam used and the compression levels applied [20,185]. It is likely that changes to fabrication parameters may be needed when 'scaling up' fabrications, and there may not be a 'one size fits all' style best approach. A comparative evaluation of gradual compression, vacuum bag compression and controlling internal compression using rods would, nonetheless, highlight advantages and disadvantages and aid selection and adaptation of the most appropriate method for fabricating large samples of auxetic foam.

Alternatives to the thermo-mechanical fabrication process [9] include using a solvent or softening agent instead of heating. Acetone [196] and pressurised CO₂ [21] can be used, depending on polymeric constitution and types of bonding present within the original foam. Softening methods can be combined, and both acetone [2] and CO₂ [21] have been used in combination with heat. Chemicals can be used to target specific bonds (i.e., SAN particle bonds) [20]. Liquid solvents (such as acetone) will require a drying phase and so some form of gradient is likely in larger samples. Provided there is no significant gradient due to diffusion of gases from the centre of samples during/after fabrication, the CO₂ softening route could reduce the effect of temperature gradients in thermo-mechanical fabrications.

Attempts to apply thermo-mechanical fabrication methods typically used for open cell foam to closed cell foam can rupture the foam's cell walls [185,198]. NPR has still been achieved along one axis in closed cell low density polyethylene (LDPE) foam, by combining thermal softening (at 110 °C) and high hydrostatic pressure (662 kPa, applied by a pressure vessel) over 10 h and maintaining the pressure for a further 6 h after cooling [199]. Heating for an hour at 86 °C, then subjecting to vacuum pressure for 5 min prior to sudden restoration of atmospheric pressure also produced uniaxial NPR in the same LDPE closed cell foam [199]. Slow diffusion of gas through cell walls was similar to predicted values, suggesting the cell walls in the auxetic LDPE foam had remained intact. Solid state foaming (sticking together pieces of closed cell foam cut in a re-entrant shape) [200], syntactic foam processes (embedding degradable/collapsible beads with a re-entrant shape into a molten/liquid polymer) [201] and AM [202] have also produced auxetic foam-like structures.

Measuring strain in compliant, often inhomogeneous foam or foam like structures requires non-contact methods. Wide ranging studies, employing a variety of test protocols, have been undertaken to characterise auxetic polymeric foams for structural, mechanical, thermal, filtration Appl. Sci. 2018, 8, 941 9 of 33

and impact properties, for example. Isotropic auxetic foams with Poisson's ratio between 0 and -0.7 have been reported (e.g., [3,9,20,22,23,189,195,203]). Higher magnitudes of NPR (<-1) have also been reported for anisotropic auxetic foams [187,190]. Density measurements of whole or dissected samples are useful in assessing the extent of, and variation in, volumetric compression throughout thermo-mechanically fabricated re-entrant foam [22,204]. Standardisation while characterising samples would help assess levels of agreement between different studies. Where possible future testing should be undertaken in accordance with, or based upon, the appropriate ASTM standard (e.g., ASTM-D412—15a [205]) for quasi-static tensile testing, which requires communication of sample dimensions, strain rate, range and measurement method and joining/contact methods between sample and test rigs.

3.3. Fabricating Auxetic Textiles

Auxetic textiles have the potential to contribute enhanced mechanical properties to textile applications in sport—including for apparel, equipment and injury prevention and treatment. Developments of auxetic fibres and fabrics, and their production methods, have enhanced the potential to use auxetic textiles commercially. Auxetic yarn with a high magnitude of NPR (<-2) can be produced from standard, non-auxetic fibre materials and conventional textile manufacturing processes [206]. Fabrics can, therefore, be manufactured from auxetic yarns without the need to develop new techniques.

The auxetic yarn in Reference [206] comprises a relatively high modulus thin wrap fibre around a lower modulus thick core. Both wrap and core components are typically conventional fibres. When extended the (initially helical) wrap fibre becomes straight and pushes the (initially straight) core fibre into a helix. Since the core is thicker than the wrap, the final stretched yarn is thicker with the helix core than the initial un-stretched yarn with a helical wrap. Due to the double helix nature of the wrap and core construction, the auxetic yarn is referred to in the literature as the double helix yarn (DHY) [207] and also the helical auxetic yarn (HAY) [208–211]. In this review we refer to this yarn as the DHY. Development of the DHY includes an auxetic plied yarn [212], auxetic braided structure [160], and a DHY where the 'wrap' fibre is stitched in place to offer more control over its behaviour by preventing fibre slippage [213]. Heat treatment has also been utilised to solve the issue of slippage [214]. The initial angle at which the wrap fibre is spun around the core fibre, and the diameter ratio of wrap to core fibre influences the value of the NPR, whereby a lower yarn wrap angle increases the magnitude of NPR [215–217]. The DHY offers increased energy absorption under impact [209].

The production of auxetic polymeric monofilament fibres has also been reported and utilises a process of continuous melt extrusion [218,219] to form a microstructure of interconnected surface-melted powder particles. NPR arises at the microscale of these monofilaments, in contrast to conventional filaments, for which mechanical properties, including Poisson's ratio, arise at the molecular (polymer chain) level [220]. The developed auxetic monofilaments have been used to demonstrate enhanced fibre pull-out resistance of auxetic fibres, requiring double the extraction force (than their conventional counterparts) [221], which could enhance the longevity and robustness of sports apparel and equipment.

Auxetic yarns and fibres have been incorporated into fabrics. The DHY has been employed to produce auxetic woven fabrics for composite reinforcement [206] and potentially as medical bandages [217]. Auxetic plied yarns have also been used in woven fabrics where yarns with shorter floating threads promote a greater magnitude of NPR in the fabric [222]. The auxetic monofilament has been used to develop knitted, woven and non-woven fabrics [223].

Auxetic fabrics can also be produced from conventional fibres. Out-of-plane NPR has been induced in non-woven fabrics, produced thermo-mechanically [224,225], via compression between two flat, heated plates to tilt and buckle needle punched fibre bundles. The through-the-thickness auxetic samples consist of bent fibre bundles perpendicular to the surface of the fabric. Under tension, the bent fibre bundle becomes re-orientated, in turn pushing on surrounding fibres and causing the fabric

Appl. Sci. 2018, 8, 941 10 of 33

thickness to increase. More recently, auxetic foldable woven fabrics have been fabricated through the use of conventional yarns and weaving technologies [226].

Knitting technologies offer the benefit of a high structure variety [29], enabling the fabrication of a range of different geometrical auxetic textile patterns. Auxetic fabrics can be manufactured using conventional yarns on commercial warp knitting machinery, which can be produced at rates and quantities comparable to non-auxetic warp knits [227]. Hexagonal structures are used for NPR warp-knitted textiles, including a rotational hexagonal structure [228] and re-entrant hexagonal net structures [229]. These hexagonal meshes have since influenced the fabrication of in-plane auxetic spacer fabrics (Figure 4a) [230,231]. Auxetic spacers exhibit excellent shape fitting to complex curves [232], high energy absorption and indentation resistance, and these properties could be enhanced with a greater magnitude of NPR [233]. Yarn loading capacity in NPR spacers affects tensile energy absorption [234], and FEM has successfully predicted the tensile NPR of a warp-knit spacer fabric [166]. Further research and tailoring of NPR spacers could aid the fit of sporting PPE that covers dome-like surfaces, such as protective head-wear [232].

Auxetic weft-knitted fabrics have also been fabricated with computerised flat knitting machines, based on three geometrical structures; (i) foldable structures (Figure 4b); (ii) rotating rectangles and (iii) re-entrant hexagons [235]. When using conventional yarns, the fibre type and geometrical structure are critical to the NPR of these fabrics and they can be adapted to tailor their Poisson's ratio and elastic modulus. Large NPRs (<-1) are possible, depending on the structure and yarns employed [235]. Auxetic foldable weft-knitted textiles have also been used as the reinforcement in polymeric composite materials [236]. Developments of auxetic weft-knitted fabrics will find a wide variety of potential applications in different fields, such as PPE for sportswear and headwear, but more research needs to be undertaken to explore these potential applications further [29].

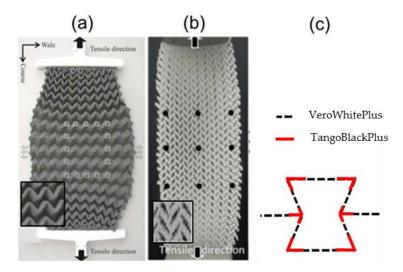


Figure 4. (a) Points marked on auxetic warp-knit fabric under tension [36]; (b) NPR effect of a weft knit fabric subject to extension [29]; (c) Dual-material auxetic metamaterial.

3D auxetic textiles have been developed for composite reinforcement applications [5,237]) through the use of warp and weft yarns [238] with stitch yarns [239] and auxetic fibres [240]. A four layer woven 3D auxetic textile structure has been used as composite reinforcement through a vacuum-assisted resin transfer moulding process [241]. Charpy impact tests (ASTM D6110-17 [242]) found the energy absorption of the auxetic textile was 6.7% higher than that of its conventional counterpart [241]. 3D Auxetic textiles have also been employed to reinforce a foam matrix fabricated by injecting and foaming [243,244]. With through-thickness NPR, 3D textiles may soon provide the enhanced protection associated with NPR materials to sports apparel and PPE [5].

Appl. Sci. 2018, 8, 941 11 of 33

There has, then, been a significant increase in the development and variety of auxetic fabrics since 2011. Due to the range of auxetic textiles under development and their unusual properties, these materials have a wide variety of potential applications [14]. For sports apparel, auxetic textiles could enhance comfort and performance in PPE, with the unique ability to fit easily to curved shapes combined with high compressive energy absorption and indentation resistance [245]. In order to implement auxetic textiles commercially, a future focus should be given to factors affecting their usage and wearability [246]. To embed or incorporate auxetic materials into sports garments, they should be relatively soft and flexible, lightweight, breathable and mouldable or available in a variety of shapes and thicknesses (5 to 10 mm). They may also be required to be homogeneous and/or joinable using flat lock seams [83].

3.4. Additively Manufactured Auxetic Materials and Structures

As alternatives to often inhomogeneous foams or textiles, the creation of auxetic materials with repeatable structures using various AM techniques has been investigated (e.g., fused deposition modelling [137], selective electron beam melting [175], selective laser sintering [247] and lithography-based ceramic manufacturing [248]). AM is a natural extension of FEM, as the existing modelling file can be converted to be compatible with most AM technologies to fabricate the modelled structure [167,249–252]. The AM structure can be experimentally tested to validate and potentially improve FEM [162,253–255], and key parameters can consequently be tuned and investigated with a particular application in mind.

Example materials used for AM in auxetic research include compliant rubbers and plastics. Metals and ceramics can also be made via AM but these studies have been omitted due to their incompatibility with sporting PE and PPE. Auxetic 3D chiral lattices have been modelled and produced by AM using TangoBlack® (Stratasys, Eden Prairie, MN, USA), a rubber-like AM filament [256]. AM has also combined two materials of different stiffness within; (i) one re-entrant unit cell [202,257,258] (Figure 4c); and (ii) novel chiral auxetic structures consisting of four 'base' unit cells surrounding a smaller 'core' chiral unit cell [259]. Using two materials of different stiffness provides a designer with greater control over unit cell deformation. The chiral auxetic has since been developed to use a re-entrant cell as the 'core' unit cell [260], meaning softer hinges are not necessary and the structure can be made from one filament material. The location and amount of each dual material provides additional ways to tune the mechanical properties (e.g., stiffness) of a structure without changing its geometry; as illustrated with the FEM of layered auxetic plates [261]. FEM and AM used in conjunction could facilitate such a parametric study with relative ease, for example by varying repeated structures [262].

AM structure's Poisson's ratio can be tuned by altering the geometry of a unit cell [263–265], enabling the design and analysis of novel auxetic structures using FEM [266,267] to help validate existing analytical formulae. Matlab has also been used to run FEM parametric analysis [167]. NinjaFlex $^{\mathbb{B}}$, (Ninjatek, Manheim, PA, USA) an elastic and flexible thermoplastic PU, has been used in the AM of auxetics [137,268–270], and in impact testing studies [269,270], with FEM used to highlight auxetic structures' desired shock absorption capacity. Elsewhere, impact testing on non-auxetic NinjaFlex $^{\mathbb{B}}$ honeycombs demonstrated that increasing strain rates (0.01 to 0.1 s $^{-1}$) resulted in an increase of energy absorbed (0.01–0.34 J/cm 3) [271]. Both strain rate and energy absorption are key considerations for auxetic material applications in sporting PE and PPE.

3.5. Gradient Materials

Gradient materials can be made from one material by varying its macro-structure to have different mechanical and structural properties in different regions (e.g., auxetic and conventional regions). Gradients can be discrete [22,23,272] or continuous [22,272]. Composite sandwich structures employing discretely gradient honeycombs have a higher compressive modulus and are stronger than conventional sandwich structures [41]. The same sandwich structures exhibit a large increase in bending stiffness at the transition between conventional and NPR regions [42]. Opposing synclastic/anticlastic (domed/saddled)

Appl. Sci. 2018, 8, 941 12 of 33

curvature associated with negative/positive Poisson's ratio respectively [9] cause increased shear modulus between regions and a localised stiffening effect. A similar stiffening effect can be seen in AM honeycombs with re-entrant inclusions during tensile tests [273]. Stiffening between discrete gradients of conventional and NPR could increase the bending stiffness (of the whole structure or specific regions) in sports equipment that contains honeycomb or fibre reinforced composites (e.g., skis, snowboards, tennis rackets and hockey sticks to name a few). Auxetic composite sandwich structures have not been tested for sports applications.

Gradient foams have been fabricated, by applying variable compression gradients to different sample sizes ($\sim 2 \times 2 \times 2$ cm to $\sim 30 \times 30 \times 2$ cm) using rods [22,23] and/or selecting mismatched uncompressed foam and mould shapes [22,23,272] (e.g., uniform foam sample compressed in a tapered mould). These gradient auxetic foam samples can exhibit vastly different cell structure and mechanical properties in different regions, which can be explained using an analytical model [23]. Gradient structures could be employed to foams or other materials (i.e., fabrics) to allow the development of garments which will fit to the wearer and adapt to their shape as they move.

4. Expected Characteristics and Supporting Evidence

Beneficial characteristics of auxetic materials include increased shear modulus, indentation resistance [10,30], dynamic [274,275] and static compressive energy absorption [8,37] and decreased bulk modulus [10,30]. Increased indentation resistance [30] and compressive energy absorption [2,8,33,37,204] have been shown experimentally in comparisons of auxetic and conventional foams. Lateral expansion due to axial tensile loading makes auxetic structures/materials ideal candidates for straps in apparel, increasing area to spread increasing loads and prevent 'digging in' [276]. Many of the characteristics which provide unique enhancements for auxetic materials come from Elasticity theory [10,277].

For isotropic materials experiencing elastic deformation, Young's modulus (E) and shear modulus (G) are related (Figure 5a, Equation (1)), as are Young's modulus and bulk modulus (K, Figure 5b, Equation (2)) [278]:

$$G = \frac{E}{2(1+v)} \tag{1}$$

$$G = \frac{E}{2(1+\nu)}$$

$$K = \frac{E}{3(1-2\nu)}$$
(2)

Elasticity theory states that Poisson's ratio must be between -1 and 0.5 for 3D isotropic materials [118,279,280], and between -1 and +1 for 2D isotropic materials [281]. From Equations (1) and (2), as Poisson's ratio tends towards -1 both shear (Equation (1)) and bulk (Equation (2)) modulus are driven towards extremely high or low values (respectively) in a 3D isotropic material.

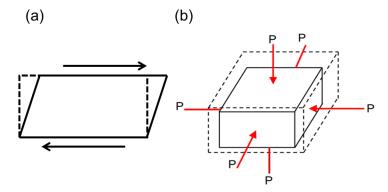


Figure 5. Schematic showing (a) shear deformation and (b) bulk/volumetric deformation. Black arrows show shear loading, red arrows show loading due to hydrostatic pressure, dashed lines show original (a) shape and (b) volume.

Appl. Sci. 2018, 8, 941 13 of 33

Indentation resistance is a measure of the load required to indent a material (Figure 6a,b). From elasticity theory, Hertzian indentation resistance (*H*, Equation (3)) for an isotropic material compressed with a uniform indenter depends on Poisson's ratio, Young's modulus and a constant (*x*) related to the shape of the indenter [31].

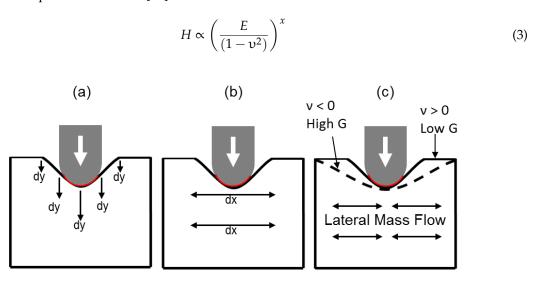


Figure 6. Simplified 2D indentation showing (a) Axial deformation; (b) Lateral deformation described in Equation (3); (c) Effect of large shear modulus (Equation (1)) on indentation area (- - -) and lateral mass flow, both un-accounted for in Equation (3). The red line shows contact area (Equation (4)).

A material with large indentation resistance, but low Young's modulus, could be used in a protective pad that will deform by a similar amount for high or low area (i.e., flat surface vs. studded) impacts. Such a pad would be more versatile, reacting to different surfaces to optimise its resistance to deformation [282]. Assuming a constant Young's modulus, as Poisson's ratio tends towards -1, a material should exhibit infinitely higher resistance to shear deformation (Figure 5a, Equation (1)) and high indentation resistance (Figure 6, Equation (3)), while becoming increasingly easier to deform volumetrically (Figure 5b, Equation (2)). Infinite shear modulus and maximum indentation resistance and volumetric compressibility can only be achieved elastically and isotropically with auxetic materials [10], and increased indentation resistance has been shown experimentally [30,31,283].

Equation (3) for Hertzian indentation resistance comes from elastic properties and assumes; (i) the surfaces are continuous and have non-conforming profiles; (ii) the area of contact (Figure 6) is much smaller than the characteristic dimensions of the contacting bodies; (iii) the strains are small and purely elastic and (iv) the surfaces are frictionless at the contact interface. These four assumptions for Hertzian indentation are not always held, although Equation (3) is often referred to and discussed in the context of non-Hertzian indentations [284,285]. Sporting PPE typically has a low thickness, so does not often meet assumption (ii). A finite thickness model has been developed for soft and thin cushion materials where Hertzian theory is expected to become invalid, and auxetic cushions were found to reduce the contact pressure on the buttocks (indenter) [286]. In another approach, Equation (3) has been adapted for thin sheets of rubber [287], to include a correctional multiplier based on a ratio of contact area between the sheet and indenter (A_t , Figure 6) and the sheet's thickness (a_t) (Equation (4)). As thickness decreases towards zero, contact area/thickness increases and the correction tends towards unity. The force required to indent rubber to a specific depth increases as thickness decreases, but it is unclear if the same trend applies to NPR materials. The final assumption of zero friction has been shown through FEM and continuum mechanics to be invalid in simulations of infield situations [285,288–290]. In these simulations, friction was found to enhance NPR's contribution to indentation resistance.

$$Correction = 1 - exp^{-\frac{A_t}{a_t}} \tag{4}$$

Appl. Sci. 2018, 8, 941 14 of 33

Equations (3) and (4) are for instantaneous, linear values. They do not, therefore, account for the different amounts of densification and possible hardening caused by lateral deformation due to Poisson's ratio (Figure 6c). Auxetic foam (with a relatively high shear modulus, Equation (1)) should resist shear deformation more than its conventional counterpart. Auxetic foam's upper surface would, therefore, compress as a larger, flatter area (represented by the dashed line, Figure 6c) as shown in cylindrical indentations [30] and using FEM [291]. FEM and analytical models also report a reduction in contact area for simulations with NPR materials [292], suggesting that deformation occurred over a larger radius, rather than the foam wrapping around the indenter. The opposite effect (auxetic foam wrapping around the indenter) has been predicted in FEM simulations of low strain indentation of 2D linear-elastic isotropic blocks [183] and also observed during impacts with a hemispherical dropper onto samples covered with 1 to 2 mm thick polypropylene sheets [3]. In the FEM study, a lower Young's modulus as well as NPR was employed for the auxetic foam, providing a shear modulus almost a factor of 2 lower than the conventional foam (Equation (1)), which possibly explains the discrepancy. In the experimental study, the added complexity when considering multi-material systems (e.g., featuring a stiff shell and compliant foam), hemispherical or studded indenters (rather than cylindrical) and high strain rates caused by impact could explain the observed differences. The relationship between the shell and foam's elastic moduli (as discussed in relation to coatings [293,294]), the foam's Poisson's ratio [292,294] and synclastic/anti-synclastic (domed or saddled) bending in the upper surface may affect indentation resistance.

Hertzian indentation requires corrections for high strain indentations, impacts of non-linear materials or multi-material systems typical in sporting PPE [47,48] and, therefore, testing of auxetic foams for sports applications [285,288]. As noted above, friction (assumption iv) is expected to amplify increases in indentation resistance caused by NPR [285,288], and a correction factor has been applied [288]. Experimental indentations of auxetic materials, particularly foams, are not common [7,30], although some limitations of Hertzian indentation theory have been noticed and discussed [30]. Further significant modelling and experimental research examining NPR's effect on indentation responses of conforming, non-linear, anisotropic materials subject to a range of indenter sizes and shapes is therefore required.

One of the difficulties in testing NPR's effect on expected benefits (i.e., impact force attenuation or indentation resistance) when using foam is changes to Young's modulus and stress-strain relationships following fabrication [9,295]. Studies report auxetic foams with lower initial Young's modulus than their conventional counterparts [189,274,295]. Reduced Young's modulus has been attributed to the presence of buckled ribs in the auxetic foam being easier to deform than the straighter ribs of the conventional foam [295]. Elasticity theory (Equation (1), Figure 5a) also supports a reduction in Young's modulus as Poisson's ratio decreases if shear modulus remains constant. Auxetic foams typically have a higher density than their open cell parent foam, so the reduction in Young's modulus is contrary to the usual expectation of an increase in Young's modulus with increased density [118]. Note, though, that Gibson and Ashby refer to a density increase caused by thicker ribs, whereas in the auxetic foam fabrications density increases due to changes in rib orientation. Gibson and Ashby's cellular solid theory actually indicates that Young's modulus can either increase or decrease when moving from a hexagonal to a re-entrant cell geometry, characteristic of auxetic foams [118]. The increased Young's modulus is allowed by elasticity theory—materials with the same bulk modulus (Equation (2), Figure 5b) will have increased Young's modulus as Poisson's ratio decreases. Increases [2,190,197,204] as well as the aforementioned decreases in Young's modulus [9,274,295] have been reported in auxetic foam fabrications.

The re-entrant structures in auxetic foams typically give an initially quasi-linear compressive stress-strain curve, with hardening as pores close at higher compression levels (>~50%) [9,183,185,275,282]. Conventional open cell foams exhibit a low-stiffness plateau region due to buckling of cell ribs between ~5% and 80% strain (Figure 7a) [118]. Both of these cases have been explained numerically and validated experimentally [23,118]. It should be noted that the relatively linear and plateauing

Appl. Sci. 2018, 8, 941 15 of 33

stress-strain relationships only apply to specific forms of cellular materials that adapt a re-entrant structure, including PU foams [9,23] and 2D honeycombs [96]. Exceptions have been recently presented; re-entrant auxetic PU foams with a plateau region [23,195].

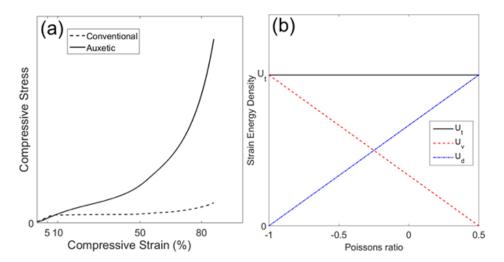


Figure 7. (a) Typical compressive stress vs. strain response of auxetic and conventional open cell foam (note cellular collapse between 5 to 10% then hardening beyond 80% strain via densification in open cell foam); (b) Strain energy density (Volumetric (U_v , Equation (5)), Distortion (U_d , Equation (6)) & U_t , Total) vs. Poisson's ratio for a linear elastic isotropic material subject to a uniaxial stress. Uniaxial stress and Young's modulus set to 1 kPa.

For a linear elastic isotropic material subject to a uniaxial stress (σ), the total strain energy density (U_t) is the sum of the volumetric strain energy density (U_v) and the distortional strain energy density (U_d), which are related to the Young's modulus and Poisson's ratio (i.e., [278]):

$$U_v = \frac{(1-2v)\sigma^2}{6E} \tag{5}$$

$$U_d = \frac{(1+v)\sigma^2}{3E} \tag{6}$$

In Figure 7b, an applied compressive uniaxial stress and Young's modulus are arbitrarily equated to 1 kPa for simplicity. Plotting these values in Equations (5) and (6) between elastic limits of -1 and 0.5 for Poisson's ratio (Figure 7b) shows an increase in volumetric strain energy density and a reduction in distortional strain energy density as Poisson's ratio tends towards -1. Auxetics material's tendency to volumetric (rather than distortional deformation) could effectively increase indentation resistance (Figure 6c, Equations (3) and (4)). As Poisson's ratio decreases, so does the stress concentration at a crack's tip, preventing crack propagation and increasing toughness [296,297]. Von Mises and maximum shear stress theory both define failure when distortional strain energy exceeds a maximum value. The reduction in distortional strain energy (to zero, Figure 7b) as Poisson's ratio reduces to -1 [279] is, then, expected to lead to an increase in toughness. A natural example of where this may be exploited may be found in the nacre layer of certain seashells. Nacre has a reported tensile NPR of the order of \sim 0.1 [93] and \sim 0.4 [298] which is thought to increase volumetric strain energy density by \sim eleven times while more than halving distortional strain energy density, allowing the system to absorb more energy before failure [298].

Increased energy absorption has been shown experimentally for auxetic foam; under flat plate [33] and studded impacts [274], quasi-statically with flat compression plates [8], within aluminium tubes [299] and with a studded indenter and a stiff shell [7]. When compressed cyclically at high strain rates (0.036 to $0.36 \, {\rm s}^{-1}$ [300] and $0.033 \, {\rm s}^{-1}$ [2,274]) auxetic foams absorbed up to sixteen times more

Appl. Sci. 2018, 8, 941 16 of 33

energy than open cell foams of a different polymeric composition and equivalent density, therefore appearing more useful in cushioning layers of sporting (and general) PE & PPE. The differences in energy absorption do not account for changes in stress/strain relationship or strain rate dependency between conventional and auxetic samples. As strain rates increased, Young's modulus and the magnitude of NPR increased marginally in samples of auxetic PU foam [301]. In some cases the increased linear elastic range of the auxetic foam compared to the parent foam with a plateau region in the stress-strain relationship could have contributed to higher energy absorption [2,8,33].

Energy absorption, strain rate dependency and (often) indentation resistance combine to influence performance under impact. Theoretically beneficial for impact protection [282], auxetic foam samples have been shown to exhibit between ~three and ~eight times lower peak force under 2 to 15 J impacts adapted from BS 6183-3:2000 for cricket thigh pads [3,8,55]. During a comparison of high strain rate compression (20 to 40 J) to a conventional commercial foam of similar density, auxetic samples exhibited (1.2 to 1.8 times) higher peak acceleration, but also exhibited higher compressive elastic modulus [2]. Peak forces can be further decreased (1.2 to 1.5 times) during 5 J impacts by impregnating auxetic foam with shear thickening fluid [302].

Inward material flow has been shown under impact by rudimental visual inspection of high-speed camera stills, and the samples with the greatest magnitude of NPR exhibited higher lateral contraction, lower through thickness deformation and a similar peak force to other samples [33]. Newly developed 3D auxetic textile composites exhibit lower peak forces than their conventional counterpart under 12 to 25 J impacts [5]. In helical yarns, a wrap angle of 27° gave the best combination of Poisson's ratio and stiffness for energy absorption [209] during 7 to 65 J impacts.

Honeycomb sandwich panels with auxetic cores were found to resist ballistic impacts better than regular or rectangular cores [303], and absorb more impact energy when the re-entrant cell structure was non-uniform [304]. Laminated composites containing warp knit auxetic Kevlar[®] fabric reinforcement, under 167 m/s impact with a 14.9 g bullet (~200 J), showed similar energy absorption to laminates containing conventional woven Kevlar[®] reinforcement [305,306]. The auxetic Kevlar[®] laminates, however, displayed enhancements in fracture toughness (225%) and fracture initiation toughness (577%), and a reduction in front and rear face damage area [305,306]. Auxetic composite laminates displayed reduced back face damage during 7–18 J impacts by a stud [32,307,308]. Auxetic composite laminates could, therefore, improve the durability of protective shells in PPE and other sports equipment (i.e., bicycle frames or boat hulls).

Related to energy absorption, auxetic foams have been tested for vibration damping (to ISO 13753 for vibration protecting gloves [309]). At low frequencies (<10 Hz), auxetic foam exhibited lower transmissibility than iso-volume open cell samples made from the parent foam and iso-density uni-axially compressed samples [193]. Auxetic foam had a lower cut off frequency than its parent foam [310]. The transmissibility of auxetic samples was greater than 1 between 10 and 31.5 Hz, but less than 1 over 31.5 Hz [183], equivalent to commercial anti-vibration gloves. Auxetic foams also fatigued uniquely, with higher permanent compression than their parent foam and a general increase (as opposed to the conventional foam's decrease) in measured hardness after 80,000 cycles up to \sim 120 N (150 mm sided cubic samples) [311].

Curvature of a beam or plate subject to an out-of-plane moment is related to Poisson's ratio [9,312]. Sheets with a positive Poisson's ratio will adopt a saddled shape (anticlastic curvature, Figure 8a) and those with NPR will dome (synclastic curvature, Figure 8b). Doming is caused by axial (due to loading) and lateral (due to Poisson's ratio) extension on the upper surface combined with equivalent contractions on the lower surface. Conventional materials will contract laterally on the upper surface and expand laterally on the lower surface.

Appl. Sci. 2018, 8, 941 17 of 33

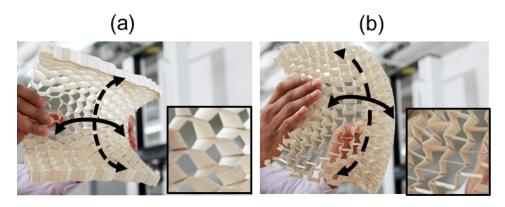


Figure 8. (a) Conventional honeycomb showing saddled curvature; (b) Re-entrant auxetic honeycomb showing domed curvature. Solid arrows show applied bending and dashed arrows show bending due to Poisson's ratio. Enlarged pop outs show cell structure.

Synclastic curvature has been observed in auxetic foam [9], analysed in detail in sandwich structures with an auxetic honeycomb core and auxetic laminate skins [312] and demonstrated by FEM [37,313] and experimentally using a simple paper model [37]. Auxetic fabric can conform around a spherical surface [36]. Deformation shape could be complicated to predict in nonlinear and often inhomogeneous auxetic foams [4]. Bespoke complex curvatures are achievable for gradient honeycombs displaying conventional and NPR regions when subject to an out-of-plane moment [314].

Some auxetic PU foam samples have been shown to exhibit shape memory, meaning they return to their original dimensions when heated [315] or exposed to solvents [196]. Shape memory auxetic foams investigated by heating in an oven returned rapidly towards their original dimensions when the temperature reached 90 $^{\circ}$ C. Samples had reached their original dimensions by the time the oven reached the original fabrication temperature of 135 $^{\circ}$ C.

Marginally re-entrant structures with NPR which exhibit partially blocked shape memory have been fabricated [195]. The fabrication process included numerous cycles of thermo-mechanical fabrication followed by reheating to return samples towards their original state. Auxetic behaviour was found in 'returned' samples from the third returned stage onwards, and has been attributed to the presence of kinked or corrugated ribs. Clearly shape memory could be detrimental in terms of sport safety equipment, as pads could be changed irreparably when exposed to heat or solvents (i.e., when machine washed or dried). Blocking shape memory [195] or investigating solutions to prevent a return to original dimensions (such as constraining auxetic foam in an outer textile/shell layer) could improve a product's lifecycle.

Several characteristics change in the auxetic foam fabrication process, including Poisson's ratio, stress/strain relationships and density [3,4,8,9,23,185,190,316]. So, during comparative impact tests between auxetic and parent foam [2–4,7,8,33,204,316], the specific contribution of individual characteristics, including Poisson's ratio, can be difficult to determine, and unambiguous experimental verification of theoretical enhancements due to the NPR requires further work. The same can be said for other studies into auxetic foam, including those into vibration damping [183,193], resilience/strength [317] and energy absorption [37].

Comparing results from scientific literature suggests that the compressive Young's modulus (30 to 50 kPa) of auxetic open-cell PU foams [3,4,118,185,316] is typically more than twenty times lower than that of the closed cell foams often found in sporting PPE (~1 MPa) [43,47–49,52]. Such a large reduction in stiffness suggests that the two materials are not comparable and stiffer auxetic foam is required for sporting PPE. The enhancements provided by NPR (e.g., indentation resistance) might allow for some reduction in stiffness, but to absorb an equivalent amount of energy to current sporting PPE, current auxetic foam would need a contribution from having NPR that would increase energy absorption by ~twenty times. The largest reported increase in energy absorption for auxetic vs. conventional foam

Appl. Sci. 2018, 8, 941 18 of 33

is sixteen times during dynamic cyclic tests [300], but increases of ~three times are more common in single impacts/compressions [8,33,204]. Crash mats are typically softer than PPE (~50 kPa [59]) and (due to their extensive variety of possible applications and impact scenarios) could benefit from the increased energy absorption and indentation resistance associated with auxetic foams [7]. The authors are not aware of any publications specifically comparing impacts or indentations of auxetic foam to foam typically found in sports PE and PPE.

5. The Potential for Auxetic Materials in Sports Products

The sporting goods sector is characterised by early uptake of new technologies and rapid product development, launch and replace cycles. Consequently, this sector is amongst the first to see commercial products based on auxetic materials, with two commercial sports shoe ranges that utilise auxetic structures. The Under Armour Architech sports shoe range [28] incorporates either an AM or moulded auxetic re-entrant latticed upper (Figure 3a) which is claimed to aid conformability around domed shapes, fit and comfort. The added manufacturing benefit of being formable as a one-piece upper, rather than several pieces each individually cut to shape and stitched together is also claimed. The Nike Free RN Flyknit sports shoe [34], on the other hand, employs an architectured closed cell foam outsole with an auxetic rotating triangles structure (shown in Figure 9, first proposed in [105–107]). The outsole is claimed to exhibit bi-axial growth as the wearer accelerates or changes direction, for improved traction and impact energy absorption.

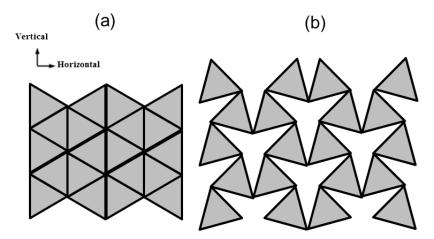


Figure 9. Schematic showing (a) rotating triangles (un-deformed); (b) rotating triangles' multi axial expansions (rotation = 15°), tensile load applied either vertically or horizontally.

Multi-axis expansion (due to NPR) has potential benefits in cleaning/shedding of dirt [39]. Multi-axis expansion could be implemented in a conformable facemask [35] to protect against extreme weather during outdoor/adventure sports, or commuter cycling—expanding bi-axially when the mouth is opened to increase breathability [9,38–40]. Other benefits of multi-axis expansion include large volume change, allowing design of small, easily stored garments which can expand when worn (i.e., for spare layers in outdoor/adventure sports).

D3O market the Trust Helmet Pad System [318] incorporating pads with a re-entrant auxetic geometry that are claimed to provide increased fit to the head and decreased acceleration under blunt impact. More products are likely to emerge if the increased level of comfort and protection offered by auxetic materials can be further demonstrated, justifying investment in the development of stiffer, more appropriate auxetic materials (such as closed cell [199] or shear thickening fluid impregnated [302] auxetic foams, or novel impact hardening auxetic polymers [319]). The emergence of sports products including auxetic materials could be assisted by the development of a commercially-viable (low cost, large scale) auxetic foam production process [23,185,186]. 'Felted' foams, fabricated by uniaxial

Appl. Sci. 2018, 8, 941 19 of 33

compression, are already commercially produced and exhibit auxetic behaviour in one loading direction [33]). Alternatively AM is a commercially viable option [28] to provide fine control over unit cell structure for auxetic foam-like structures.

The ability to change the shear modulus of a material through Poisson's ratio [118,151] could provide a useful tool in designing head protection that can reduce rotational acceleration [6]. When used in place of a comfort layer in a helmet, auxetic foam can significantly reduce the severity of direct impacts in comparison to its conventional counterpart [320]. Helmets and helmet certification standards have been criticised for focusing solely on direct rather than both direct and oblique impacts [69]. Controlling shear modulus by changing Poisson's ratio (to negative or positive values) of any layer within the helmet could contribute to solutions to reduce rotational acceleration (i.e., in combination with or instead of slip plane technology [77]). The benefit of using Poisson's ratio to change shear modulus is that elastic moduli would change less, limiting the effect on linear acceleration and therefore perceived performance according to current certification standards [66,67].

6. Conclusions

In a competitive, rapid uptake market such as sports equipment, it is important to keep searching for new and improved designs and materials. With frequent, catastrophic high-profile injuries and scandals (particularly involving head injury) the importance of improvement increases. The chance to increase market revenue, while reducing costs to health services, national economies and burdens on injured individuals, warrants continued research through commercial and state investment.

Auxetics have a wide range of potentially useful characteristics, including increased indentation resistance, vibration damping and shear modulus as well as decreased bulk modulus. These have been shown using auxetic foam compared to its parent foam and iso-density conventional foams. Further experimental comparisons of auxetic and conventional foam's indentation resistance, impact force attenuation and vibration damping are required to determine contributions from other variables, such as elastic modulus and density, to clearly identify the contribution due to Poisson's ratio.

The creation of auxetic foams appropriate and beneficial to sporting goods will require development of fabrication processes, especially for larger samples. Fabricating samples with comparative characteristics (e.g., Young's modulus and density) is also required to show the NPR's benefits (i.e., to indentation resistance). The solvent and CO₂ softening routes provide alternative and, in the latter case, faster auxetic foam fabrication. Increasing the stiffness of auxetic foam closer to the closed cell foam found in sporting PPE or ensuring that impact energy absorption is equivalent or higher is an important step for commercialisation. With dynamic energy absorption reported up to sixteen times greater in auxetic foams some reduction in stiffness is likely acceptable, but requires confirmation by appropriate testing. AM presents an alternative for the creation of auxetic cellular solids with bespoke properties. There is increasing confidence, then, that commercial auxetic foam production will be achievable, either by AM or by improved fabrication methods from open cell foams. Commercially available auxetic foam would improve access, allowing more sport safety equipment manufacturers to design, test and evaluate auxetic prototypes.

Another option to increase auxetic materials range of moduli and impact force attenuation is combining materials. Auxetic foam's impact force attenuation increased up to ~1.5 times when supported by shear thickening fluid. Enhancing the characteristics of auxetic fabrics and textiles by combining with a conventional, gradient or auxetic material could facilitate the production of sports garments and performance apparel that deforms with the wearer and attenuates impact forces. Combining conventional and auxetic sections of honeycombs in gradient sandwich structures increases bending stiffness close to transitions. Snowboards, skis, tennis rackets and hockey sticks (to name a few) use conventional sandwich structures, and could benefit from increased rigidity or equivalent rigidity and lower mass.

The more obvious characteristics of auxetic materials that are backed up with strong supporting evidence (multi axis expansion and domed curvature) have been implemented as auxetic foam and AM

Appl. Sci. 2018, 8, 941 20 of 33

materials into sporting footwear and helmet pad products. Commercial success for auxetic sporting PPE requires stronger supporting evidence that responds to trends accurately re-creating infield collisions and falls. Other auxetic materials such as laminates and knitted/woven fabrics that exhibit characteristics including increased fracture toughness and, potentially, tailorable shape change, are currently untested for sports applications within the peer-reviewed scientific literature. Unlike auxetic foam production, the fabrication of auxetic composite laminates and many of the auxetic fabrics is via established commercial processes, requiring little or no modification. With further development and testing auxetic laminates and fabrics could be applied to a range of sporting products, from carbon fibre reinforced composite bicycle frames to swim suits or rugby tops that deform with the movements of the wearer.

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Appl. Sci. 2018, 8, 941 33 of 33

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