Review On auxetic materials

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Although a negative Poisson's ratio (that is, a lateral extension in response to stretching) is not forbidden by thermodynamics, for almost all common materials the Poisson's ratio is positive. In 1987, Lakes first discovered negative Poisson's ratio effect in polyurethane (PU) foam with re-entrant structures, which was named anti-rubber, auxetic, and dilatational by later researchers. In this paper, the term 'auxetic' will be used. Since then, investigation on the auxetic materials has held major interest, focusing on finding more materials with negative Poisson's ratio, and on examining the mechanisms, properties and applications. Therefore, more materials were found to have the counter-intuitive effect of auxeticity due to different structural or microstructrual mechanisms. The present article reviews the latest advances in auxetic materials, their structural mechanisms, performance and applications. © 2004 Kluwer Academic Publishers

1. Introduction

Generally, there are four constants used to describe the material's elastic behavior: the tensile (or the Young's) moduli (E), the shear moduli (G), the bulk moduli (K) and the Poisson ratio (ν). Poisson's ratio is defined as the ratio of a lateral contraction to the longitudinal extension during stretching of a material for specified directions. For isotropic material, the four constants are dependent as Equations 1 to 4 [1].

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

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

$$E = \frac{9KG}{(3K+G)} \tag{3}$$

$$\nu = \frac{1}{2} \left(\frac{3K - 2G}{3K + G} \right) \tag{4}$$

Most structural materials are required to have a higher G than K. If we can change the microstructure of a material in a way that E remains constant but ν changes, we can alter the values of K and G. For example, when decreasing ν to -1, a very high shear modulus relative to the bulk modulus was obtained [2]. Although a negative Poisson's ratio (that is, a lateral extension in response to stretching) is not forbidden by thermodynamics, for almost all common materials the Poisson's ratio is positive, being close to 1/3 for most materials and about 1/2 for rubbery materials [3].

In 1987, Lakes [3, 4] discovered the negative Poisson's ratio polyurethane (PU) foam with re-entrant structures, then such a particular phenomenon was named anti-rubber, auxetic, or dilatational materials by later researchers [5]. In this paper, the term 'auxetic' will be used. Since then, investigation on the auxetic materials has held major interest, focusing mainly on finding new materials with negative Poisson's ratio, on examining the mechanisms, properties and their relationship, applications of auxetic materials were also noticeable. In 1993, Lakes [6] presented a review dealing with auxetic materials, their fabrication methods, implications of these unusual physical properties, and research advances from his discovery. After that, more new materials were found to have the counter-intuitive effect of negative Poisson ratio due to different structures and deformation mechanisms. This effect results in many specific properties of these materials, which may lead to more applications of them. The present article reviews the latest advances in auxetic materials, their structure and deformation mechanisms, performance and applications.

2. Auxetic materials

Till now, a range of auxetic materials have been discovered, fabricated, synthesized or theoretically predicted, such as polyurethane and polyethylene foams prepared by Lakes [3, 4, 7], Evans [8–11] and others [12], microporous polytetra-fluoroethylene (PTFE), microporous ultra high molecular weight polyethylene (UHMWPE) and polypropylene (PP) fabricated by Evans *et al.*

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[13–15], highly anisotropic composites [16], laminates [17, 18], and several types of rocks [19, 20] with microcracks. Naturally occurring molecular auxetic α -cristobalite [21], zeolites [22] were also predicted to process the counter-intuitive property by calculation or simulation.

2.1. Auxetic cellular solids

Auxetic polyurethane foams composed of reentrant cells with dimensions greater than 1 mm were firstly studied. The foams can be prepared by one stage thermo-mechanical processing including triaxial compression of conventional open cell foam into a mold, heating of the specimen slightly above the softening point of the foam material, cooling and relaxation [3] or a more controlled multi-stage processing technique separating the transformation process into several stages, which can minimize the risk of surface creasing and produce more homogeneous specimens [8]. Recently, polyethylene foams were also transformed into re-entrant microstructures through the thermomechanical processing, and obtained the auxeticity [7]. Copper foam [23], expanded polystyrene blocks (EPS blocks) [24] were also found to exhibit auxeticity, which can be incorporated in detailed analyses of various geotechnical engineering structures. The physical origin of the auxeticity of the foams can be appreciated in view of the idealized unit cell as shown in Fig. 1 and the key to achieve auxeticity in re-entrant foams lies in their microarchitecture, where the ribs of each auxetic foams' cells permanently protrude inward compared with conventional foams' convex cell structure [25].

Honeycomb structures are widely used in structural applications owing to their specific strength. Conventional honeycomb structures can be fabricated into reentrant structures. The re-entrant honeycomb structure has a negative Poisson's ratio in the cell plane with a value that depends upon the re-entrant angle of the cell rib [26]. The re-entrant cell geometries showing auxeticity can also be fabricated using femtosecond laser ablation, for instance, micromachined polymeric honeycomb membrane [27]. Except for polymer materials, the special microstructure can also be achieved in others. For example, the honeycomb ceramics with auxeticity can be produced by the extrusion of ceramic



Figure 1 Idealized re-entrant unit cell produced by symmetrical collapse of a 24-sided polyhedron with cubic symmetry (after R. Lakes [3]).

pastes through polymer dies produced by rapid prototyping (selective laser sintering) and designed with CAD technology [28]. The study of auxetic honeycombs were mainly focused on theoretic prediction of the influencing factors such as geometric effects [29], density variations [30], material constants [31] and the properties such as electromagnetic and mechanical properties [32], wave beaming effects [33], damping properties [34] and so on.

2.2. Auxetic microporous polymers

The first example of an auxetic macroporous polymer identified was a form of expanded PTFE [13]. The microstructure comprises an interconnecting network of nodules and fibrils whose cooperative interaction under an applied load produces the auxeticity. Later on, UHMWPE [14, 35–37] and PP [15] were generated through compaction, sintering and extrusion route or only sintering and extrusion processing to achieve auxeticity because the microstructure also consisted of interconnected network of nodules and fibrils. The nodules and fibrils reacted cooperatively, producing an expansion in the transverse direction, and at the same time, the fibrils caused the nodules to be pushed apart. The value of Poisson's ratio varied with tensile strain and the values as large as -6 [38], and even -12 [13] were obtained.

Besides, porous membranes could also be auxetic, Sevick *et al.* [39] discussed how porous membranes grafted by polymers could behave as valves and sensors. For chains grafted onto the surface and for internally grafted chains, densely grafted chains in good solvents form impenetrable layers, which swell under shear.

2.3. Auxetic composites

The effective Poisson's ratio of laminated fiber reinforced composites can also appear to be negative. The phenomenon was observed by controlling buckling by tailoring laminates with in plane restrained unloaded edges where Poisson's effect was predominant to the extent that caused premature instability and significant departure from classical behavior [16]. Composites prepared by laminating unidirectional prepreg tapes of epoxy resin reinforced with continuous carbon fibers, were also shown to be auxetic for θ in the range between 15 and 30° , which was in accordance with the standard laminate theory [40]. In angle-ply composites made up of unidirectional layers of glass or high-modulus carbon fibres within an epoxy resin matrix, arranged such that there are an equal number of layers at an angle to a reference direction, theoretical and experimental investigations showed a large, positive in-plane Poisson's ratio, and a large, negative out-of-plane Poisson's ratio restricted to a single sample direction [41]. Using the specific values of independent elastic constants in each lamina due to the extension-shear coupling, randomly oriented quasi-isotropic composite laminates were predicted to exhibit negative in-plane Poisson's ratio by a random statistical analysis [42].

On the other hand, composites composed of matrix and embedding voids or inclusions of different shape were theoretically or experimentally studied and some of which were also predicted to exhibit auxeticity, e.g., composites designed using a numerical topology optimization method, composing of two different material phases and void [43]. The availability of cracks narrow cut with a flat surface in a solid body resulted in the theoretical reduction of Poisson's ratio, and in some cases it might be negative [44, 45]. A numerical investigation of types of composites with voids and frameworks or composites with irregular shapes of inclusions showed that even if the constituents were quite usual materials, provided that their porosity was strongly manifested, the composites were able to exhibit auxeticity influenced by mainly the shape, and the ratio of shear-to-bending rigidity of the beams [46].

The inclusions themselves can also be auxetic components. A series of analytical studies by Wei [47– 49] demonstrated that composite materials embedding auxetic components such as spherical, elliptic or ellipsoidal, disc-, blade-, sphere-, disk- and neddle-like inclusions in an elastic material with sufficiently high modulus to improve upon relatively low Young's modulus of existing auxeticity, do be auxetic when the inclusion volume fraction exceeds a critical value and the ratio of Young's modulus of inclusion to that of a matrix falls within a definite interval.

Recently, the existence of the counterintuitive auxeticity was theoretically studied with reference to the orthorhombic CuAlNi alloy and it was shown that in the plane x_1x_3 the Poisson's ratio is always negative [50].

2.4. Molecular auxetic materials

Auxetic molecules include polymers with special microstructures [51] and special inorganic crystals as Evans [22] pointed out, e.g., silicon dioxide [21], zeolites [22], and elemental metals [52] and so on.

Fig. 2a illustrates schematically a typical example of the microstructure that produces the auxeticity. By reproducing the re-entrant geometric unit on the molecular scale, (n, m)-refexyne exhibited auxeticity as shown in Fig. 2b [51]. More recently, by molecular mechanics calculations, Wei *et al.* designed several types of centipede-like polymers, single-arrow-like and doublearrow like organic compounds as building blocks to self-assemble into auxetic network though hydrogen bonds. Again, the self-assembled networks could be arranged as inverted honeycomb like structures and their Poisson's ratio in at least one plane were negative [53, 54].

He *et al.* proposed a simple molecular design approach (see Fig. 3), based on site-connectivity driven rod reorientation in main chain liquid crystalline polymers to achieve auxetic behavior. Under a tensile force, the extension of the flexible spacers in the polymer main chain will force the laterally attached rods from a position roughly parallel to the tensile axis to a position normal to it and push the neighboring chains further apart [55].

A SiO₂ polymorph of α -cristobalite structure, unlike other silicas and silicates, exhibits auxeticity because of



Figure 2 (a) Two-dimensional re-entrant honeycomb showing transverse expansion on stretching. (b) (1, 4)-refexyne with a negative Poisson's ratio (after Evans [51]).



Figure 3 (Top) Arrangement of laterally attached rods in a main chain liquid crystalline polymer. The nematic field leads to orientation of the laterally attached rods parallel to the polymer chain axis. (Bottom) Under tensile stress, full extension of the polymer main chain forces the laterally attached rods normal to the chain axis. If the laterally attached rods are sufficiently long, the interchain distance could increase, leading to an expansion in the direction normal to the chain axis and hence to auxetic behavior (After He *et al.*)[55].

the cooperative rotation of SiO₄ molecular tetrahedral with the framework structure. Tensorial analysis of the elastic coefficient shows that Poisson's ratio reaches a maximum value of -0.5 in some directions, whereas the average values for the single-phased aggregate yield a Poisson's ratio of -0.16 [21].

Zeolites are another important class of polyhedral framework nanostructures and are commonly used as molecular sieves because of their availability and their well-defined molecular-sized cavities and pathways. From force-field-based molecular modeling calculations, several idealized zeolitic cage structures were predicted to possess the auxeticity. In most of these idealized molecular structures, the auxetic behavior could be explained through a combination of the framework geometry and simple deformation mechanisms existing within the framework [22].

The 'opalized forms' of a novel phases of carbon of diamond and graphitic foams-cubic phases 'rectangulated carbon phases,' a hexagonal acetylenic carbon phase and related polytypes, and hinged carbon phases were also found to be auxetic [56]. In contrast to the general belief that auxeticity is rare in crystalline solids [57], 69% of the cubic elemental metals exhibit when stretched along the 110 direction [52]. For example, the compliance coefficients s₁₁ and s₁₂ of single crystals of Zn are of the same sign. Consequently, for $\theta = 0$, $v_{12} = -s_{12}/s_{11}$ approximately equals -0.073 < 0, the Poisson's ratio of monocrystalline Zn in its basal plane is negative [58]. For these metals, the auxeticity permits the existence, in the orthogonal lateral direction, of positive Poisson's ratios up to the stability limit of 2 for cubic crystals. Such metals were predicted to be able to make electrodes that amplify the response of piezoelectric sensors [52].

Boulanger [59] gave a simple artificial example to illustrate that for orthorhombic materials with positive definite stored energy density, Poisson's ratio need not be bounded either above or below—it may be arbitrarily large and positive, or arbitrarily large in absolute value but negative.

3. Structure and deformation mechanisms 3.1. Auxetic cellular solids

A reentrant cell shape, discovered by Lakes in 1987 [3, 4], was a defined foam structure with which the material exhibited auxeticity. The physical origin of the auxeticity can be interpreted by above-mentioned Fig. 1. Tension applied to the vertical links will cause the cell to unfold and expand laterally. The actual cell structure also contains ribs, which are bent and protruded into the cells. The three-dimensional unit cell was modeled as an idealized polyhedron unit cell of isotropic foam structures. From the model, it was found that the Poisson's ratio was a function of strain, and tended to approach the isotropic limit of -1 with increasing permanent volumetric compression ratio and the experimental Poisson's ratio were as small as -0.8 [60]. By altering the cell shape of open-celled foams, it is possible to achieve different values of the elastic constants and different degrees of anisotropy. It was shown that simple two-dimensional approximations failed to model the properties of the three-dimensional network accurately and a full three-dimensional analysis was required. The reentrant cell used is fully auxetic when located in all three orthogonal directions [61]. Based on the formulation of strain-energy function accounting for stretching which is the main deformation mechanism in this material, a hyperelastic nonlinear model for light and compliant open cell foams with an explicit correlation between microstructure and macroscopic behavior was presented. In the model, bending, shear and twisting energies were all incorporated [62].

Broken cell ribs in auxetic foams were experimentally observed and based on this phenomenon, a twodimensional model, missing rib foam model, with one form being a network of ribs with biaxial symmetry and another form being similar network but with a proportion of cell ribs removed, was found to be superior in predicting the Poisson's function and marginally better at predicting the stress-strain behavior of the experimental data than earlier models, using realistic values for geometric parameters. The model was found to be able to describe the strain-dependent Poisson's function behavior of honeycomb and foam materials [63].

For auxetic honeycombs, based on the deformation of the honeycomb cells influenced by flexure, stretching and hinging, Evans *et al.* developed a theoretical model to predict the elastic constants of honeycombs and derive expressions for the tensile moduli, shear moduli and Poisson's ratios. It was shown the elastic properties could be tailored by varying the relative magnitudes of the force constants for the different deformation mechanisms. Depending on the geometry of the honeycomb the properties may be isotropic (for regular hexagons) or extremely anisotropic. Again, the degree of anisotropy was also affected by the relative magnitude of the force constants for the three deformation mechanisms, flexure, stretching and hinging [64].

Huang et al. [31] derived a 2-D triangular finite element formulation including an extra degree of freedom on the basis of Eringen's micropolar elasticity theory by using a linear triangular element to investigate the relation between the Poisson's ratio of a re-entrant honeycomb structure by varying the micropolar material constants such as micropolar Young's modulus, micropolar Poisson's ratio, characteristic length, coupling factor, and micropolar elastic constants in accordance with the micropolar elastic restrictions. According to the numerical results [29], the honeycomb structure could exhibit auxeticity with the appropriate re-entrant angle and the Poisson's ratio values varied when changing the honeycomb structure cell rib length and width. Generally, the larger the cell rib width was, the greater the values of structural Poisson's ratio were and the Poisson's ratio of the structure could become negative even if the Poisson's ratio of intrinsic material was positive. If a load was applied along the long cell rib length of a honeycomb structure, the variation in the Poisson's ratio becomes more obvious.

Research of the effect of varying the rib thickness on the mechanical properties of conventional and reentrant periodic honeycombs investigated by Finite Element modeling, found that the mechanical properties varied not only with honeycomb relative density, but also with the relative density variation. Reducing the thickness of 'vertical' ribs, whilst maintaining constant 'diagonal' rib thickness, did not alter the Young's modulus and Poisson's ratio in the x direction (E_x and v_{xy}), but did lead to a decrease in the magnitude of the ydirected properties (E_y and V_{yx}). Reducing the diagonal rib thickness at constant vertical rib thickness led to a more marked decrease in E_y as well as in E_x , whereas v_{xy} and v_{yx} both increased in magnitude. The results had implications for applications in which maximising or maintaining mechanical properties with respect to relative density is important [30].

3.2. Auxetic microporous polymers

Simple geometric node-fibril (NF) models were firstly developed for axetic microporous PTFE (see Fig. 4) in which a regular array of rigid square or rectangular nodules was formed into a connected network by freely hinged inextensible rods (fibrils). These models



Figure 4 (a) SEM photograph of sheet material showing fibril network and anisotropic particulate nodes (*x*, horizontal and *y*, wertical axes) (after K. E. Evans [13]). (b) An example of the microstructure of auxetic UHMWPE, displaying the characteristic nodules and fibrils (after K. E. Evans [14]).



Figure 5 Schematic diagram of structural changes observed in microporous PTFE undergoing tensile loading in the *x* direction: (a) Initial densified micro-structure, (b) tension in fibrils causing transverse displacement of nodes and lateral expansion, (c) rotation of nodes producing further lateral expansion, and (d) fully expanded condition, prior to plastic deformation due to node break-up (after K. E. Evans [13]).

(see Fig. 5) comprised a transverse translation model describing the movement of the nodules caused by the fibrils becoming taut, bringing out a lateral expansion, and a rotation model describing the rotation of nodules producing further lateral expansion. Deformation of the network, by hinging of the fibrils in response to an applied load, resulted in positive and negative straindependent Poisson's ratios, depending on the geometry of the network [65-69]. When the models were applied in microporous UHMWPE, it was found that the translation mechanism agreed very well with the experimental data, while the rotation mechanism wasn't suitable, which showed that the interconnectivity of the microstructures was the principal factor determining the measured Poisson's ratio of UHMWPE. Therefore, as stated in an investigation [70] on elongation mechanism, the auxetic region was believed to be characteristic of PTFE in contrast to common polyethylene and other polymers.

Later, the NF model was extended to a concurrent node-fibril model including flexure and stretching of the fibrils. The tensile NF network for microporous polymers with a regular array of rigid rectangular nodules interconnected by hinged rods (fibrils) to the *x*-axis can deform by hinging, flexure and stretching of the fibrils. A combination of the hinging mode followed by the stretching mode of deformation can be used to explain the general features of the experimental data, and the use of concurrent deformation mechanisms makes a very significant improvement in the agreement of theory with experiment for PTFE and UHMWPE [36].

For auxetic microporous polymers with straindependent Poisson's ratio, Alderson *et al.* presented a simple geometric model allowing the possibility of tailoring Poisson's ratio of the material. The model included rectangular nodules interconnected by fibrils. The auxetic UHMWPE processed to yield a very wide range of Poisson's ratios depending on its microstructural parameters (i.e., nodule shape and size, fibril length and the angle between the fibril and nodule) could be interpreted using the model successfully [35].

The factors influencing the auxeticity of microporous polymers generated by the thermal processing route of compaction, sintering and extrusion were systematically studied in UHMWPE [38, 71, 72]. It was found that while the compaction stage imparted structural integrity to the processed polymers, the conditions such as compaction temperature, stand time, loading rate, compaction pressure and loading time for optimizing the production of auxetic UHMWPE were not identical to those for optimum structural integrity of the compact [71]. The optimum sintering conditions (temperature and time) to produce the microporous microstructure necessary for the auxeticity were also identified [28]. In the third stage of extrusion, investigation on the effects of die geometry (cone semi-angle, exit diameter and capillary length) and extrusion rate on the ability of the polymer to produce an auxetic extrudate, found that a delicate balance must be achieved between the production of an extrudate which lacked structural integrity and extrudate which was solid but possessed a conventional positive Poisson's ratio, and did not exhibit the nodule-fibril microstructure necessary for auxetic behavior. In conjunction with the results from the series of results, the authors defined a set of conditions required to produce auxetic UHMWPE [72]. Later on, the compaction stage of the processing route was omitted. The effects of varying the processing parameters of the sintering and extrusion stages were studied so that a set of conditions that produced a highly fibrillar auxetic material with sufficient structural integrity to allow mechanical properties to be evaluated could be defined and Poisson's ratios as low as -4 were obtained [73].

In polypropylene fabricated in the way similar to that used for the production of auxetic UHMWPE, it was demonstrated that powder morphology such as particle shape, size, and surface roughness were critical variables for successful processing to achieve auxetic behavior [15].

3.3. Auxetic composites

Continuum materials with specific microstructural characteristics and composite structures have been confirmed to be able to exhibit auxeticity analytically [74]. It has been proved to be valid for certain mechanism involving beams or rigid levers, springs or sliding collars frameworks and, in general, composites with voids having a nonconvex microstructure [75]. For microstructures composed of beams, it had been postulated that nonconvex shapes with re-entrant corners were responsible for the auxetic effect [76]. A detailed numerical study showed that the shape of the re-entrant corner of a non-convex, star-shaped (Fig. 6), microstructure influenced the phenomenological Poisson's ratio. The same is valid for composites with irregular shapes of inclusions, even if the individual constituents are quite usual materials. Elements of the numerical homogenization theory were used for the numerical investigation [75].

For laminates, if two plies with different fiber orientations are stuck together, they have the same deformation when forces are applied. An internal shear will be developed in the plies to coordinate the deformation. When the internal shear stress exerts to the off-axis ply, it will induce an extension because of the shearextension coupling character. It is that extension which may widen the specimen and cause the development of a negative in-plane Poisson's ratio in the laminate [42]. The effects of fiber orientation and aspect ratio were well documented, and it is possible to control buckling

Figure 6 A periodic fiber-reinforced composite with star-shaped encapsulated inclusions (After P. S. Theocaris [75]).

by tailoring laminates to exhibit auxeticity and proper selection of boundary conditions in the design and optimization of composite plates [76].

When investigating the transverse elastic moduli of a unidirectional composite material reinforced with identical multilayered hollow-cored fibers are evaluated by the use of a multiphase generalized self-consistent model, it was found that the effective transverse Poisson ratio of some numerical examples for composites reinforced with thinly coated hollow-cored fibers, and with osteon-like fibers, becomes negative beyond certain porosity levels, and that the parity of the number of fiber layers is a significant parameter [77].

3.4. Auxetic molecules

The structure and deformation behavior of auxetic polymer molecules [50, 55] as mentioned above is presented in Figs 2 and 3 and will not be discussed again here.

The auxetic behavior in tetrahedral framework silicates was also identified. Both the positive and the negative Poisson's ratio, observed in α -quartz and α cristobalite were explained by concurrent tetrahedral rotation and dilation. The concurrent model was in good agreement with the experiment and explained the dichotomy between the negative and positive values [78].

An idealized isotropic system consisting of rigid squares connected together at their vertices by hinges was modeled to achieve a negative Poisson's ratio of -1 regardless of the direction of loading. Since many examples of crystalline materials have such geometry, it was envisaged that auxetic behavior in crystals through this mechanism was highly probable [79].

The force-field-based molecular simulations, carrying out through a combination of the framework geometry and simple deformation mechanism acting within the frameworks, were used to predict the auxeticity in idealized zeolite cage structures. The presence of cations and molecular-sized pores in the structure of zeolites helped to study their potential as molecular auxetics. The relation between the effect of geometry and deformation mechanism on framework nanostructures and the auxetic behavior of idealized zeolite structures were depicted as Fig. 7 [22].

When auxetic cubic elemental metals were stretched along the 110 direction, it was found that correlations exist between the work function and the extreme values of Poisson's ratio in this stretch direction (see



Figure 7 (a) The idealized rotating "hinging squares" mechanism of auxetic rotating squares. (b) The idealized model for achieving auxetic behavior from hinged rotating rigid equilateral triangles, and the different configurations may be obtained by loading in a uniaxial direction (after K. E. Evans [22]).



Figure 8 The structural origin of a negative Poisson's ratio and a giant positive Poisson's ratio for the case of a rigid-sphere b.c.c. solid (after Ray H. Baughman [81]).

Fig. 8). The correlations were explained using a simple electron-gas model. Moreover, this auxeticity permitted the existence, of positive Poisson's ratios up to the stability limit of 2 for cubic crystals in the orthogonal lateral direction [80]. In auxetic monocrystalline phases, molecular-mechanics calculations for some hypothetical phases of carbon were derived from the presence of bonds acting as hinges in extended helical chains, and Baughman pointed that such structures could be envisaged for polyacetylene, polydiacetylene, polyphenylene and (BN)x phases, as well as for variants of some known, structurally related inorganic phases [81].

4. Unique properties of auxetic materials

It is important to understand interactions within the material structure that give rise to auxeticity, and it is also necessary to study the overall behaviors of these novel materials as pointed out by Lakes [59].

Auxetic Materials demonstrate the fascinating property of becoming fatter when stretched, which is fundamentally important to the properties of a material and a significant change in Poisson's ratio has significant effects on the materials' mechanical performance. The auxetic materials present some unique properties in comparison with the common materials. For example, classical elasticity theory predicts that auxeticity of materials should lead to enhancements in certain mechanical properties, such as increased plane strain fracture resistance and increased shear modulus [28], indentation resistance [11, 82, 83], fracture toughness [3, 84, 85], and acoustic response [86] compared to conventional materials. In this section, properties resulting from auxeticity of materials were involved.

4.1. Mechanical properties

The static, elastic shear modulus and the dynamic loss tangent were found to increase with the auxeticity of the foam theoretically and experimentally, which was attributed to the changes in the geometry of microstructure of the foam and so the deformation characteristics [9, 10, 87], while the Young's modulus of aux-

etic honeycomb structure decreased as the inverted angle of cell ribs increased [26]. A combined analysis of the out-of-plane mechanical and dielectric properties of auxetic re-entrant honeycombs was performed versus the core material and unit cell geometry parameters, and the results showed that auxetic honeycombs offered increased transverse Young's modulus compared to analogous regular hexagonal honeycombs with the same relative density [32]. Recently, Experimental study and numerical simulations were carried out by Scarpa to evaluate the correlation between the anisotropicity of the transverse mechanical properties (shear and compressive modulus) and the permittivity tensor of auxetic honeycombs. The results were evaluated to assess the feasibility of this kind of cellular solid for electro-magnetic absorption and window applications with high structural integrity performance [88]. In the composites with great auxeticity, considerably enhanced transverse moduli could be achieved without altering the longitudinal moduli. For example, changing the matrix Poisson's ratio from 0.3 to -0.9and keeping all other constituent properties constant produced an almost four-fold increase in the composite transverse modulus [89].

Although it was theoretically predicted that auxeticity of materials would result in improvement in fracture toughness, the property was seldom studied. The fracture toughness was explored experimentally as a function of permanent volumetric compression ratio, a processing variable. Critical J-integral (J_IC) values of the auxetic open cell copper foams were enhanced by 80 percent, 48 percent, and 160 percent for permanent volumetric compression ratio values of 2.0, 2.5, and 3.0, respectively, compared to that of conventional foam with a positive Poisson's ratio. Analytical study based on idealized polyhedral cell structures approximating the shape of the conventional and re-entrant cells disclose for re-entrant foam, toughness increasing as the Poisson's ratio became more negative. The increase in toughness was accompanied by an increase in compliance, a combination not seen in conventional foam, and which may be useful in some applications such as sponges [84]. Higher notch fracture strength was obtained in unbalance laminates with negative Poisson's ratio by a study on the near-tip stress fields for crack and stress intensity factors [85].

4.2. Indentation behaviors

The indentation resistance of auxetic copper foams investigated by holographic interferometry showed that the re-entrant foams had higher yield strengths σ_y and lower stiffness *E* than conventional foams of the same original relative density [82], which was attributed to the deformation characteristics of re-entrant (concave polyhedral) cell structures [11]. When experimentally verifying the strain dependent densification of auxetic foams, Smith *et al.* found that the auxetic specimens had enhanced indentation resistance independent of bulk density and modulus. The auxetic foams did densify under indentation, and the strain field under the indenter was much larger, probably due to enhanced shear stiffness [90].

The indentation resistance of auxetic microporous UHMWPE was a strain dependent property, and the hardness was be improved by up to a factor of 2 over conventional UHMWPE for the presence of auxeticity [83]. At lower loads (from 10–100N), where the resistance to local indentation was most elastic, indentation test showed it was more difficult to indent and the least plastic with the most rapid viscoelastic creep recovery of any residual deformation and the hardness was increased by up to a factor of 8 on changing the Poisson's ratio from approximately 0 to approximately -0.8. This was interpreted by local densification under the indentor of the nodules and fibrils [14, 91].

4.3. Deformation behaviors

In fact, all kinds of properties of auxetic materials are related to, and are interpreted with the deformation behaviors. The deformation behaviors mentioned here only includes the studies directly aimed to the deformation of auxetic materials.

Experimental study of auxetic copper foam showed that inhomogeneous, non-affine deformation because of non-uniform microscopic distribution of strain which gave rise to the highest viscoelastic loss tangent due to higher strain in the lossy, compliant phase than in the composite, occurred in the ribs of copper foams, and non-affine deformation was characteristic of auxetic foam materials [92]. The mciro-deformation, of the re-entrant copper foam with a negative Poisson ratio of -0.8, investigated by double-exposure holographic interferometry, demonstrated a larger inhomogeneous deformation and hence micro-deformation in the generalized continuum sense, in a particular kind of re-entrant foam than in the conventional foam [93].

For cellular solids, Masters and Evans [64] allowed the cell ribs to deform in one of three ways: hinging about their corners, flexing along their lengths, or stretching in tension. Further development of similar cellular geometry based models allowed concurrent deformation mechanisms [36], as mentioned above.

4.4. Viscoelastic properties

A finite element method microstructure models for calculating the static and viscoelastic properties of closedcell and two-phase foam composites, demonstrated that the static and storage modulus of two-phase composite foam were significantly improved for the presence of a re-entrant skeleton layout. The loss factor also had a significant sensitivity to the volume fraction and strain energy distribution on the microstructure unit cells. Static and free-vibration simulations on sandwich beams with different core cellular materials showed that it was possible to obtain both enhanced stiffness per unit weight and modal loss factors using two-phase cellular solids with a re-entrant skeleton [34].

Investigation on the viscoelastic properties of a special kind of composites with re-entrant auxetic copper foam matrix and high-loss-filler materials such as viscoelastic elastomer, solder, and indium, showed that the loss tangent of the copper-elastomer composite substantially exceeded the Voigt limit; the loss tangent of the copper-solder and copper-indium composites were close to the Hashin limit for the two-solid phases and one-pore phase [94].

4.5. Other properties

Auxetic materials also show other superior properties such as damping, absorption behaviors than common materials with positive Poisson's ratio.

The specific damping capacity of auxetic foam with extreme compressive pre-strain was higher than that of the conventional foam, and the auxetic foam exhibited non-linear hysteresis behavior at high cyclic strains, regardless of their initial levels of pre-strain. The effect was attributed to the rubbing of the inwardly buckled cell ribs of the transformed foam [95]. Auxetic foams absorbed better than the unconverted foams at all frequencies and smaller pore-size auxetic foams absorbed sound more efficiently at frequencies above 630 Hz than those with larger pores, and those auxetic uncovered foam were better sound absorbers in the frequency range 61–1000 Hz than the uncovered [96, 97]. From a micromechanical model of the cut-off frequency based on the resonance of ribs which might be straight, curved, or convoluted, it was found that as foam cell ribs became more curved, the cut-off frequency decreased [97]. The highest measurable ultrasonic attenuation value of auxetic microporous UHMWPE was 1.5 times the highest value for the microporous positive Poisson's ratio UHMWPE and more than 3 times that for the conventionally processed material [37, 91].

Lakes presented an example of slow decay of stress arising from self-equilibrated stress at the end of a circular cylinder of elastic auxetic material. By contrast, a positive Poisson's ratio sandwich panel containing rigid face sheets and a compliant core exhibited slow stress decay for core Poisson's ratio approaching 0.5. In sandwich panels with stiff but not perfectly rigid face sheets, slow decay of stress was known to occur, while the auxeticity resulted in end stress decay, which was faster than it would be otherwise [98].

In a combined analysis by Scarpa [32], it was found that the transverse shear moduli showed increased sensitivity versus auxeticity, which was significant for the relative transverse permittivity in the z direction with increased dielectric anisotropy, while regular hexagonal honeycombs did not allow for the distinct variation of the anisotropy of the composites. These properties of auxetic honeycombs provided more degree of freedom to design globally optimized low observable aerospace components, and also allowed radomes and other electromagnetic structures to be more closely tailored to a specific application.

The crashworthiness qualities of auxetic polyurethane foam was found to be greatly enhanced comparing with normal open-cell foam by a high strain rate compression test with a constant speed of 1.5 m/s [99].

5. Applications of auxetic materials

Lakes pointed out that applications of auxetic materials might be envisaged based on the Poisson's ratio, on the superior toughness, tear resistance, or on the acoustic properties of the materials [100]. For example, auxetic materials have a promise as robust shock absorbers, air filters, fasteners, aircraft and land vehicles, and electrodes in piezoelectric sensors [52, 101]. Foams with curved or convoluted ribs were found to provide dispersion of acoustic waves and cut-off frequencies, which might lead to applications involving the absorption of sound [91]. Stress decay according to Saint Venant's principle could occur more or less rapidly as the Poisson's ratio decreased [100].

The use of the auxetic cellular solids in the design of a press-fit fastener was systematically studied. Insertion of the fastener was facilitated by the lateral contraction of auxetic materials under compression, while removal of the fastener was resisted by the corresponding elastic expansion under tension [102]. Auxetic foam was also used in the development of seat cushions, which was based on the scaling up of the processing of auxetic foam [103]. Seated pressure distribution became more favorable with decreasing sample density for auxetic foam blocks, and at densities between 0.032 and 0.064 g/cm³, auxetic foams performed better (lower maximum seating pressure) than conventional foam samples of comparable density [104]. An analytical investigation [105] found that auxetic cushions might be beneficial in the prevention of pressure sores or ulcers in the sick and in reduction of pressure-induced discomfort in seated people. Recently, an earphone having a drive unit carried by an earphone shell and covered by an ear cushion of auxetic foam was invented, which was more readily to mould around irregularities in the shape of the ear and reduce air leaks [106].

Auxetic materials and structures from the macroscale (polymeric foam) to the nano-scale (zeolites) have the potential to create filters with and enhanced pore size and with shape 'tuneablity', which could be used in filter systems providing enhanced de-fouling and pressure compensation properties [27]. In 1999, a method of separating, at least part of one or more components, from a mixture of components was provided. The method comprised exposing the mixture to a porous barrier, the barrier being formed of a material structure having, or behaving in the manner associated with auxeticity. In this way, particularly through the use of auxetic materials, improved separations, improved de-fouling of barriers and a variety of other beneficial properties could be obtained [107].

Honeycomb auxetic ceramics was manufactured by the extrusion of ceramic pastes through polymer dies produced by rapid prototyping (selective laser sintering). Ceramics with cellular or honeycomb structures have applications as substrates in catalytic converters for the emissions from internal combustion engines. In such devices due to the extreme temperature variations, the structure has to provide high thermal shock resistance. It is possible to increase the thermal shock resistance by incorporating specific web geometries, which can absorb or compensate for compressive and tensile stresses generated in the body during thermal expansion and contraction [28].

The use of auxetic polymers has been limited because of problems with deploying them in their fabricated forms, i.e., as 10 mm diameter cylinders. Recently, Alderson et al. [108] reported the successful development of a processing route to produce a more useful and usable form of auxetic polymeric material-fibers. Conventional polymer processing technique-melt spinningwas used as the basis of the technique, with novel modifications. In a recent patent, they claimed the auxetic material could be made into filamentary or fibrous form by a suitable process involving cohering and extruding heated polymer powder. Typically the powder was heated to a temperature sufficient to allow some degree of surface melting yet not high enough to enable bulk melting. It was claimed that the materials could be used as reinforcing fibers, or in textile structures, e.g., as fiber reinforcements (as Evans [2] considered years ago) in composite materials used as vehicle body or car bumper; in combination with other materials for personal protective clothing or equipment in the form of crash helmet, projectile-resistant or bullet proof vest, shin pad, knee pad or glove, filter, rope or cord formed from twisted fibers of auxetic, fishnet, replacement biomaterial, a bandage or wound pressure pad, and seal or gasket. The invented material had an enhanced energy absorption properties and fiber pullout resistance. Textile structures incorporating or made from the inventive filaments or fibers had enhanced indentation properties and low velocity impact resistance [109].

Recently, the auxeticity of piezocomposites attracted much attention, e.g., a piezocomposite consisting of piezoelectric rods embedded in an optimal polymer matrix, using topology optimization method to design the porous matrix microstructure, exhibited auxeticity [110]. Also, an optimal matrix from weakening the polymer by an optimal arrangement of pores with PZT rods embedded in, is highly anisotropic and characterized auxetic using the methods of homogenization theory in certain directions [111]. Multilevel iterative optimal design procedures were also used for the optimal material design of composite material structures including materials with special microstructure, which may lead eventually to phenomenological, overall auxeticity [112]. In the case of piezoceramic hydrophone composites, auxetic matrices were utilized to produce highly sensitive, miniaturized sensors. Envisions of such devices have promising new application areas such as the implantation of hydrophones in small blood vessels to monitor blood pressure [98]. The shape, volume fraction, and spatial arrangement of the piezoceramic rods, and the structure of the matrix material of piezoelectric composite hydrophones consisting of parallel piezoelectric rods embedded in a porous transversely isotropic polymer matrix, maximized the hydrophone performance characteristics and the optimal composite of a hexagonal array of rods with small volume fraction, in a highly anisotropic auxetic matrix in certain directions [113]. And auxetic metals were believed to be able to find application as electrodes that amplified the response of piezoelectric sensors [52].

The flow and filtration control could impart to membranes through the adsorption of auxetic polymer brushes which swelled under shear and as a result behaved as sensors and valves controlling the flow and filtration through the pore, onto the interior pores. The valve-behavior of brushes adsorbed onto cylindrical pores was found to display the same constant discharge control but also exhibits a critical shear rate for brush swelling [114].

6. Conclusion

Nowadays, it has attracted many scientists to concern about the auxetic materials due to its unique behavior. Much attempt has been made to explore not only materials with auxeticity, the mechanics the property comes from and the manufacturing methods, but also the mechanical, indention, deformation, viscoelastic properties and other functional characteristics results from the auxeitcity. With these fundamental researches, the applications of auxetic materials show a very bright potential.

One area attracting increasing interest is the development of molecular auxetics. The molecular design, on the molecular scale, incorporating nanotechnology, is highly possible to lead to a range of auxetic nanomaterials. These materials are expected to lead to high modulus auxetic materials as well as having potential in sensor, molecular sieve, separation technologies and other fields.

Aside from the functional aspect, the auxetics also show a great potential to be used as structural materials. For example, the microporous auxetic polymer materials prepared with special designed processing route by Evans and co-workers present good strength and modulus. The auxetic hierarchical composites [115, 116], the auxetics designed on the molecular scale [51, 53], are also possible to be used as structural materials.

The invention of auxetic fibers by Alderson [109], leading to a wide range of applications and improved properties, shows the most exciting foreground of industrial applications of this kind of special materials.

It is believed that significant progress could be reached for this kind of materials in the future in the theoretical and practical aspects, guiding the materials design for more applications, and more stiff and strong auxetic materials will come forth for human beings.

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