Scientific Research and Essays Vol. 5 (10), pp. 1052-1063, 18 May, 2010
Available online at http://www.academicjournals.org/SRE
ISSN 1992-2248 © 2010 Academic Journals

Full Length Research Paper

A review on auxetic structures and polymeric materials

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Accepted 29 April, 2010

Auxetic polymeric materials are a special kind of materials that exhibit negative Poisson's ratio (NPR) effect. They get fatter when stretched and thinner when compressed. Auxetic behavior is a scale-independent property which can be achieved at different structural levels from molecular to macroscopic levels. The internal structure of material plays an important role in obtaining auxetic effect. Because of NPR effect, auxetic polymeric materials demonstrate a series of particular characteristics when compared with conventional materials. In recent years, a variety of auxetic polymeric materials have been designed and fabricated for diverse applications. This article presents a review on advances in this area. The emphasis is focused on the geometrical structures and models, particular properties and applications of auxetic polymeric materials developed.

Key words: Auxetic, negative passion's ratio, modeling, structure, polymer.

INTRODUCTION

The Poisson's ratio (v) of a material is defined as the negative ratio of the transverse strain to the axial strain in the direction of loading (Wan et al., 2004). Generally, materials have positive Poisson's ratios, that is, stretching is expected to make a material thinner and compressing results in bulge. However, this common knowledge has been challenged by the auxetic materials which exhibit the very unusual property of becoming wider when stretched and narrower when compressed, that is, they possess negative Poisson's ratios (NPR) (Evans et al., 1991).

According to the classical elasticity theory, the variation scopes of v are from -1 to 0.5 (Lempriere, 1968) for three dimensional (3D) isotropic materials and from -1 to 1 for two dimensional (2D) isotropic systems (Wojciechowski, 2003a) based on thermodynamic consideration of strain energy (Fung, 1965). For anisotropic materials, the values of v could be varied in larger scopes than those of isotropic materials (Baughman et al., 1998). The variation scopes of v clearly show that the negative Poisson's ratios or auxetic effects are theoretically permissible. Although some naturally occurring materials have been discovered to have auxetic effects for a long time, such as iron pyrites (Love, 1944), pyrolytic graphite (Garber, 1963), rock with micro-cracks (Nur and Simmons, 1969; Etienne and Houpert, 1989), arsenic (Gunton and Saunders, 1972), cadmium (Li, 1976), cancellous bone (Williams and Lewis, 1982), cow teat skin (Lees et al., 1991) and cat skin (Veronda and Westmann, 1970), the auxetic materials had not drawn more attention to people until Lakes (1987) discovered that isotropic auxetic foams could be easily manufactured from conventional open-cell foam. Since then, extensive works have been done to gain insight into what makes materials auxetic and how these materials behave if compared with conventional non auxetic materials.

Auxetic materials are of interest due to their counter-intuitive behavior under deformation and enhanced properties due to negative values of v. It has been found that auxeticity can be described in terms of particular geometry of the material system and deformation mechanism when loaded (Grima et al., 2005a). The negative Poisson's ratio is a scale independent property (Grima et al., 2008a), that is, the auxetic behavior can be achieved at a macroscopic or microstructural level, or even at the mesoscopic and molecular levels.

To date, a variety of auxetic materials and structures have been discovered, fabricated, or synthesized ranging from the macroscopic down to the molecular levels. Among the works which have been done in this area, auxetic polymeric materials have widely been investigated and has drawn great attention. Currently, a large number of auxetic polymeric materials have been

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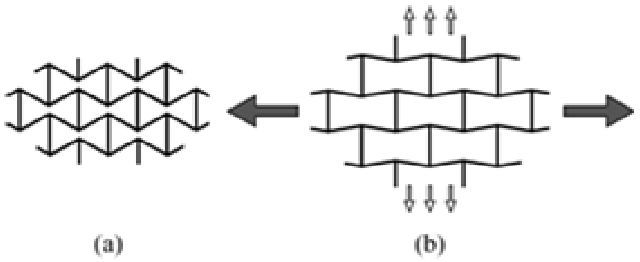

Figure 1. 2D Re-entrant honeycomb (a) Undeformed (b) Deformed.

developed in the form of foam, fiber, or even composite, including polyester urethane (PU) (Lakes, 1988; Friis et al., 1988; Lee and Lakes, 1997), polytetrafluoroethylene (PTFE) (Caddock and Evans, 1989; Evans and Caddock, 1989; Alderson and Evans, 1992, 1993; Neale et al., 1993; Alderson, 1997), ultra-high molecular weight polyethylene (UHMWPE) (Evans and Alderson, 1992; Pickles et al., 1995; Alderson et al., 1995,1998; Neale et al., 1995), polypropylene (PP) (Pickles et al., 1996; Alderson and Simkins, 1999; Alderson et al., 2002, 2005c; Ravirala et al., 2005; Webber et al., 2008; Simkins et al., 2008), nylon (Alderson et al., 1998), polyester (Ravirala et al., 2006), liquid crystalline polymers (He et al., 1998, 2005; Aldred and Moratti, 2005) and other synthetic molecular auxetic polymer (Grima and Evans, 2000b; Wu and Wei, 2004; Wei, 2005; Alderson et al., 2005a). Meanwhile, other kinds of auxetic materials based on metal, ceramic and other inorganic materials have also been developed (Evans and Alderson, 2000; Yang et al., 2004; Alderson and Alderson, 2007).

This article presents a review on auxetic polymeric materials. The emphasis is focused on the geometrical structures which can produce auxetic effects and different auxetic polymeric materials which have been developed, as well as particular properties and applications of auxetic polymeric materials. Some of special geometries which are potential to auxetic polymeric materials but have not been be used yet in the manufacture of polymeric materials are presented as well.

GEOMETRICAL STRUCTURES AND MODELS

Over the past decades, different geometrical structures and models that can result in auxetic effects have been proposed, studied and tested for their mechanical properties. Among the most important classes of such auxetic structures are 2 and 3 D re-entrant structures (Gibson et al., 1982; Lee et al., 1996; Theocaris et al., 1997; Lim, 2003; Grima et al., 2005d), chiral structures (Prall and Lakes, 1997; Spadoni et al., 2005; Bornengo et al., 2005), rotating rigid/semi-rigid units (Ishibashi and Iwata, 2000; Vasiliev et al., 2002; Grima and Evans, 2000a, 2006; Grima et al., 2005a, 2005c, 2007, 2008), angle-ply laminates (Milton, 1992; Hine, 1997), hard molecules (Wojciechowski et al., 1987, 2003; Wojciechowski and Brańka, 1989; Wojciechowski, 2003b; Tretiakov and Wojciechowski, 2005, 2007), microporous polymers (Caddock and Evans, 1989; Evans and Caddock, 1989; Alderson et al., 1998, 2007b)and liquid crystalline polymer (He et al., 1998, 2005; Aldred and Moratti, 2005).

These geometrical structures are extremely useful and important, as they can help researchers to understand better how auxetic effects can be achieved and how auxetic materials can be manufactured as well as how their properties can be optimized and predicted. A systematical review of these structures is given as follows.

Re-entrant structures

Macroscopic auxetic cellular structures in the form of 2D re-entrant honeycombs were firstly suggested by Gibson et al. (1982). As shown in Figure 1a, the honeycomb is formed with 2D re-entrant hexagons. It can be deformed by hinging of the diagonal ribs in response to an applied uniaxial load (Figure 1b). Theoretically, the alignment of the diagonal ribs along the horizontal direction when stretched causes them to move apart along the vertical direction, thereby resulting in the auxetic effect. But in reality, most honeycombs of this type of structure deform predominantly by flexure of the diagonal ribs, with occurring of hinging and axial stretching of the ribs simultaneously. Flexure of the ribs equally leads to auxetic behavior in the re-entrant honeycomb system (Alderson and Alderson, 2007).

Auxetic effects can also be obtained from other re-entrant structures, as shown in Figure 2. Opening or closing of the arrowheads and stars respectively in double arrow-head structure (Larsen et al., 1997) (Figure 2a) and star (Theocaris et al., 1997; Grima et al., 2005d) (Figure 2b) honeycomb structure due to rib flexure and/or hinging under uniaxial loading, will lead to auxetic behavior. A structurally hexagonal re-entrant honeycomb (Lakes, 1991) (Figure 2c) has been suggested to get better planar isotropic property than 2D re-entrant structure shown in Figure 1 due to structural symmetry along radical directions. However, the fabrication of auxetic materials with this structure has not been reported yet.

Other two re-entrant structures respectively formed from lozenge and square grids by eliminating some side lines in each grid are shown in Figure 2d and Figure 2e, respectively. Their repeating units (unit-cells) are highlighted in bold. The auxetic effects are obtained due to rotation and extension of each side in the unit-cells. According to the analysis (Smith et al., 2000; Gaspar et al., 2005), the structure in Figure 2e exhibits higher auxetic effect than that of the structure in Figure 2d under the same strain. Another structure is the structure formed with the sinusoidal ligaments (Figure 2f), whose auxetic effect comes from opening up of re-entrant cells into

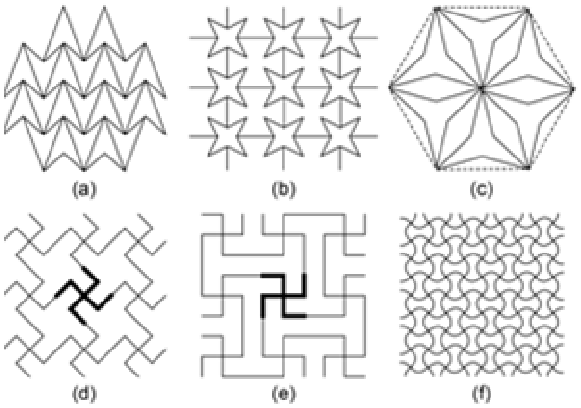

Figure 2. Re-entrant structures (a) Double arrowhead structure (b) Star honeycomb structure (c) Structurally hexagonal re-entrant honeycomb (d) Structure formed from lozenge grids (e) Structure formed from square grids (f) Structure formed from sinusoidal ligaments.
Source: Larsen et al., 1997; Theocaris et al., 1997; Lakes, 1991; Smith et al., 2000; Gaspar et al., 2005; Dolla et al., 2007.

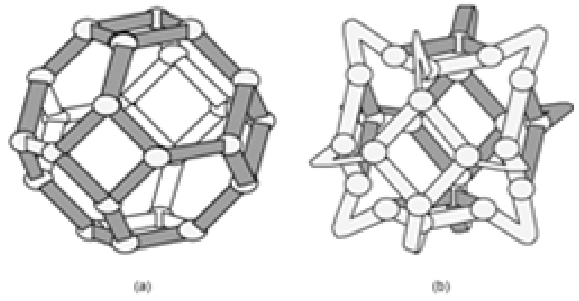

Figure 3. Three dimensional cell (a) Conventional cell (b) Re-entrant cell.
Source: Lakes and Witt, 2002.

almost rectangular cells. The rotational expansion auxetic lamina made with this structure was used for drug diffusion by Dolla et al. (2007). As an alternative, the sinusoidal ligaments can also be replaced by linear ligaments.

Besides 2D re-entrant structures, 3D re-entrant structures are also possible to get auxetic effects. As shown in Figure 3, a 3D re-entrant cell has been used to explain the auxetic behavior of auxetic foams (Lakes and Witt, 2002). This cell was produced by transformation of the conventional cell structure (Figure 3(a)) into a re-entrant cell structure (Figure 3(b)) in which the ribs protrude inwardly.

When the vertically protruding ribs are under tension, the ribs in the lateral directions will tend to move out, leading to lateral expansion. However, when compression is applied, the ribs will bend inward further, thus resulting in lateral contraction in response to axial compression. Based on this model, auxetic polymeric foams could be easily understood.

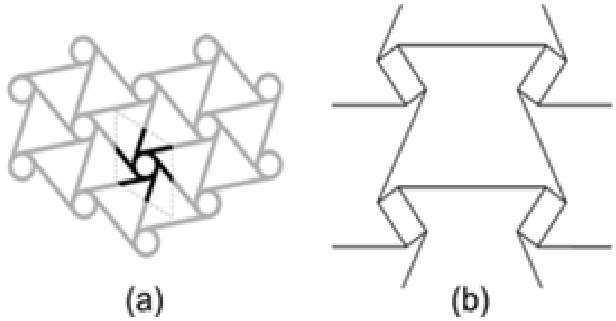

Figure 4. Chiral honeycombs (a) Formed with the same chiral units(b) Formed with symetrical chiral units.
Source: Grima et al., 2008b.

Chiral structures

Chiral structures are another kind of structures which have been developed for auxetic honeycombs. As shown in Figure 4, in this kind of structures, basic chiral units (highlighted in bold) are firstly formed by connecting straight ligaments (ribs) to central nodes which may be circles or rectangles or other geometrical forms. The whole chiral structures are then formed by joining together the chiral units. The auxetic effects are achieved through wrapping or unwrapping of the ligaments around the nodes in response to an applied force. According to the theoretical and experimental investigations performed by Prall and Lakes (1997b), Poisson's ratio of the chiral structure in Figure 4a under in-plane deformations is around -1. In contrast to most of other auxetic structures, this structure can maintain a high auxetic effect over a significant range of strains. Based on this structure, a novel class of structure referred as 'meta-chiral' (Figure 4b) has been recently developed by Grima et al. (2008b).

In this kind of structure, either the same chiral units (also called chiral building blocks) or symmetric units can be connected together to form different chiral structures. The structure in Figure 4b is formed by connecting the symmetric blocks where the node in each chiral building block is a rectangle. Though there is an infinite amount of ligaments attached to each node to form a building block, only the building blocks attached with 3, 4, or 6 ligaments may be used to construct space filling periodic structures. It is evident that the auxetic effects depend on the shape of node and the length of attached ligaments.

Rotating units

This kind of structure has been developed to produce the

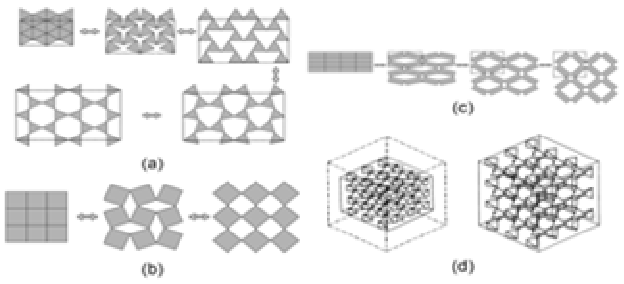

Figure 5. Rotating units (a) Triangle units (b) Square units (c) Rectangle units (d) Tetrahedron unit.
Source: Grima and Evans, 2006; Grima et al., 2005a; Alderson and Evans, 2002.

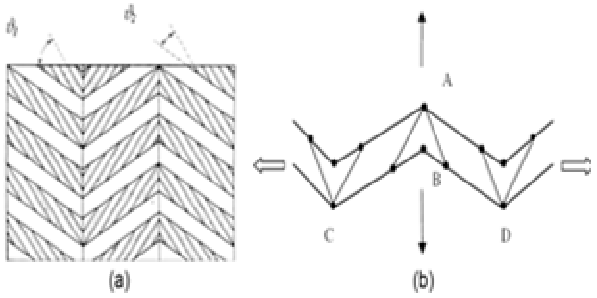

Figure 6. Auxetic composite (a) Structure (b) Model.
Source: Shilko et al., 2008.

auxetic behavior in foams (Grima et al., 2005d) and hypothetical nanostructure networked polymers (Grima and Evans, 2000a) by jointing the rigid or semi-rigid triangles (Grima and Evans, 2006) (Figure 5a), squares (Grima and Evans, 2000a) (Figure 5b), rectangles (Grima et al., 2005a) (Figure 5c) and tetrahedron (Alderson and Evans, 2002) (Figure 5d) at selected vertices. The vertices can be hinged or connected by springs. The auxetic effects come from the rotation of the triangles (Grima and Evans, 2006), squares (Grima and Evans, 2000a), rectangles (Grima et al., 2005a) and tetrahedron (Alderson and Evans, 2002) when loaded.

Angle-ply laminates

Laminated angle-ply composites have been designed and fabricated to have auxetic properties (Milton, 1992; Hine, 1997; Shilko et al., 2008). A biphasic composite material incorporating stiff inclusions and a compliant matrix as shown in Figure 6a has been proposed by Milton (1992). Hatched regions represent a compliant phase simulated by compliant tensile but flexurally rigid rods (Shilko et al., 2008). The periodicity cell is shown by a dashed line. This can be easily attained by placing a sliding element in the middle of each rod. Besides, each

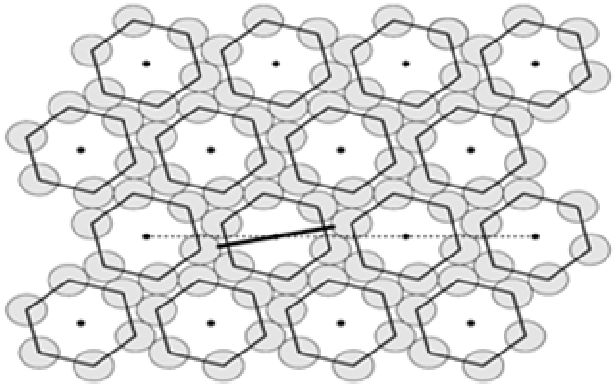

Figure 7. Geometry of the close packed structure of hard cyclic hexamers when the disc (grey colour) diameter is equal to 7/10 of the side length of the hexagon on whose vertices the disc centres are located.
Source: Wojciechowski, 2003b.

rod is replaced by a pair of parallel rigid rods fastened by two triangular links in order to retain parallelism for preventing the surfaces sliding relative to each other. The voids formed by the displacing rods to be filled by an elastic medium can obtain an auxetic composite structure with characteristic angular parameters θ_1 and θ_2.

A rod model describing the deformation behavior of such laminates is presented in Figure 6b in which the white arrows show the direction of forces and the black arrows that of shear. Under an infinitely small deformation, expansion of width AB is directly proportional to the increase of length CD. A sandwich like stack of such structures could achieve auxetic effect.

Hard molecules

Models based on rigid “free” molecules proposed by Wojciechowski (Wojciechowski, 1987, 2003b; Wojciechowski and Brańka, 1989; Wojciechowski et al., 2003; Tretiakov and Wojciechowski, 2005, 2007) are concerned with choosing the intermolecular interaction in such a way as to obtain a thermodynamically stable, elastically isotropic, auxetic phase in a system of particles interacting.

A ‘molecular’ model of cyclic hexamers (that is, molecules composed of six ‘atoms’ placed on the vertices of a perfect hexagon, see (Figure 7) was constructed and solved exactly at zero temperature and according to the references (Wojciechowski, 1987; Wojciechowski and Brańka, 1989) the phase exhibiting the negative Poisson’s ratio was proved to be thermo-dynamically stable in a range of densities at positive temperatures. The negative Poisson’s ratio of the hexamer system results only from the intermolecular interaction potential. This is in contrast to most of other works in which the Poisson’s ratio is a product of both an artificial structure of the material used and its intermolecular interaction

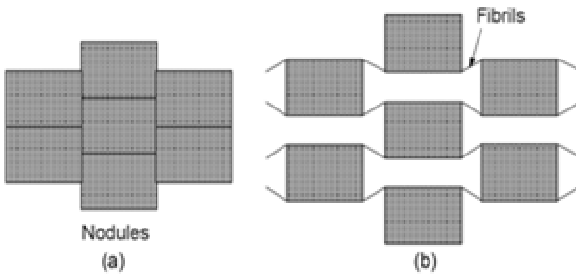

Figure 8. Schematic of nodule-fibril model representing microstructure of typical auxetic microporous polymer (a) The polymer at rest (b) The polymer at the tensile load.
Source: Caddock and Evans, 1989; Evans and Caddock, 1989.

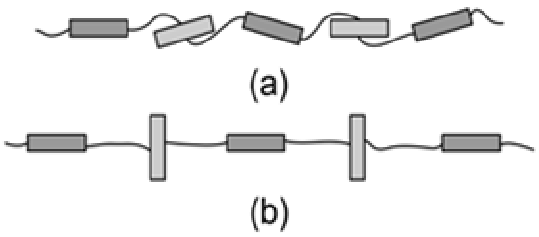

Figure 9. Theoretical liquid crystalline polymer (LCP) (a) Undeformed state (b) Deformed state due to horizontal stretching.
Source: He et al., 1998.

potential.

Microporous polymers model

For auxetic microporous polymer (Caddock and Evans, 1989; Evans and Caddock, 1989), the characteristics of the microstructure can be interpreted by a simple 2D model, as shown in Figure 8. This basically consists of an interconnected network of nodules and fibrils. If a tensile load is applied, the fibrils cause lateral nodule translation, leading to a strain-dependent negative Poisson's ratio.

Liquid crystalline polymer model

In general, molecular models have used the macroscopic re-entrant honeycomb structure as a template. In addition, auxetic behavior of these models have been predicted (Evans et al., 1995; Alderson et al., 2005a), but these structures are not realized in practice because of too heavily cross-linked (Alderson and Alderson, 2007). Recently, Griffin's group (He et al., 1998, 2005) has proposed a route to a successful molecular level polymer in the form of a liquid crystalline polymer (LCP) (He et al., 1998) due to site-connectivity-driven rod orientation in a main-chain LCP as shown in Figure 9. The LCP consists of chains of rigid rod molecules connected by flexible spacer groups along the chain lengths. The flexible spacer groups attach to the ends of some of the rigid rods connected terminally or laterally. In the relaxed state, all the rigid rods are oriented along the chain directions. Auxetic behavior occurs when the rotation of the laterally attached rods upon stretching of the LCP.

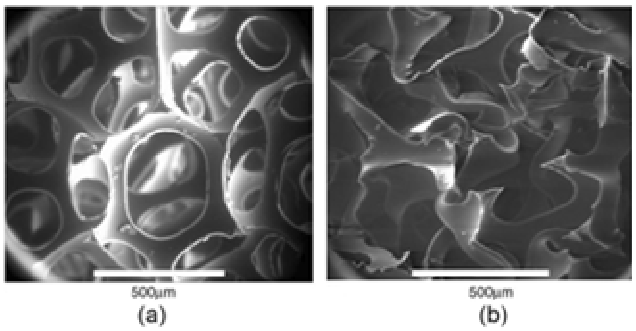

Figure 10. SEM images of PU foams (a) Conventional (b) Auxetic.
Source: Grima et al., 2006.

AUXETIC POLYMERIC MATERIALS

Auxetic polymeric materials are those designed and manufactured to have a macromolecule framework or macroscopic structures that cause auxetic behavior. So far, a series of auxetic polymeric materials have been produced in the form of foam, fiber and composite. Some molecular-level auxetic polymers have been designed, but they have not been synthesized yet.

Polymer foams

Auxetic foams have attracted considerable attention in recent years. Auxetic polyurethane (PU) foams (Figure 10) with a Poisson's ratio of -0.7 were first manufactured by Lakes (1987) using a re-entrant cell structure as shown in Figure 3. The auxetic foams could be produced from commercially available conventional foams through a process involving volumetric compression, heating beyond the polymer's softening temperature and then cooling whilst remaining under compression (Grima et al., 2006). Smith et al. (2000) converted commercially available reticulated 30 ppi PU foams which originally exhibited v of ca. +0.85 under loading to an auxetic foam which exhibits v of ca.–0.60 through a process of compression in volume by ca. 30%, heating at 200°C and then cooling in the compressed shape. Chan et al. (1997) have developed the processing routes for auxetic foams to allow scale-up to larger foam blocks, with improved process control enabling better quality (improved homogeneity and stability). A route to converting closed-cell polymer foams to an auxetic form was also reported (Martz et al., 1996). Besides PU foams, other kinds of foams could be used for production of auxetic foams. Recently, polyethylene foams were transformed into re-entrant microstructures through the thermo-mechanical processing to obtain auxeticity (Brandel and Lakes, 2001). Expanded polystyrene blocks (EPS blocks) (Preber et al., 1994) were also found to exhibit auxeticity.

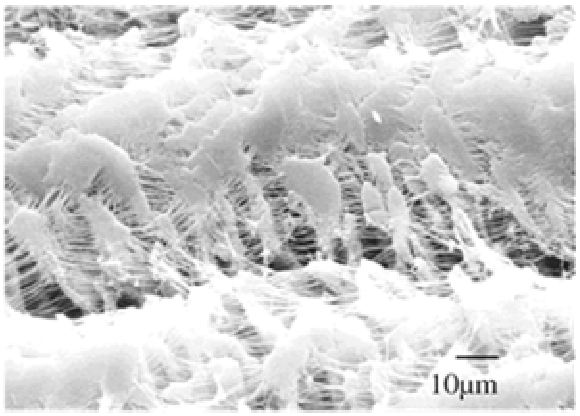

Figure 11. Nodule-fibril microstructure of auxetic PTFE. Source: Evans and Alderson, 2000.

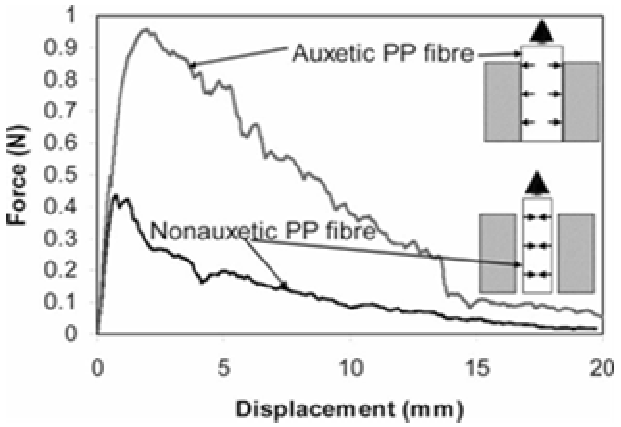

Figure 12. Single-fiber pull-out force-displacement data for auxetic and non-auxetic PP fibers embedded in epoxy resin. Inserts show auxetic fibre locking effect leading to enhanced fibre pull-out resistance.
Source: Alderson and Alderson, 2007.

The auxetic foams have been modeled in a variety of ways (Smith et al., 2000; Scarpa and Smith, 2004) such as re-entrant systems and rotating units as stated above, each model trying to reproduce some observed feature of the microscale of the foams. Such features include bent or broken ribs or inverted angles between ribs. Moreover, the properties of the auxetic foams have been extensively investigated, including dynamic, mechanical, acoustic, mass transport and electromagnetic properties (Scarpa and Smith, 2004; Scarpa et al., 2004b; Alderson et al., 2007a; Bezazi and Scarpa, 2007, 2009).

Microporous polymer fibers

The first auxetic microporous polymeric material was investigated by Evans and Caddock (1989). It was an expanded form of PTFE which has a highly anisotropic negative v = -12. Its nodule-fibril microstructure is shown in Figure 11. The auxetic effect is due to its complex microstructure which consists of nodules interconnected by fibrils. Its dominant deformation mechanism for auxetic behavior is nodule translation through hinging of the fibrils as mentioned above.

The observation of the auxetic effect in PTFE revealed that other polymers can also be processed in such a manner to produce this particular microstructure. A batch process consisting of three distinct stages of compaction (Pickles et al., 1995), sintering (Alderson et al., 1995) and extrusion (Neale et al., 1995) has been developed and used to produce auxetic microporous samples of UHMWPE (Alderson and Evans, 1992), PP (Pickles et al., 1996), nylon (Alderson et al., 1998) and polyester (Ravirala et al., 2006).

Polymeric composites

Auxetic composite materials can be produced either from conventional components via specially designed internal structural configurations or from auxetic reinforcements.

A number of theoretical and experimental studies (Herakovich, 1984; Yeh et al., 1999; Evans et al., 2004; Alderson et al., 2005b) have been done to demonstrate the possibility of producing auxetic behavior in fiber-reinforced composite laminates by conventional materials. The route is to use off-the-shelf pre-preg structure (angle-ply) which gives specific stacking sequences to produce auxetic effects. Adopting this method, composite laminates could be designed to have negative in-plane or out-plane Poisson's ratios. In order to achieve this, the requirement for an auxetic composite laminate is that the individual ply materials must be highly anisotropic (Alderson et al., 2005b). This means that carbon/epoxy (Clarke et al., 1994; Evans et al., 2004) is a more suitable choice than either Kevlar/epoxy (Al-Khalil, 1990) or glass/epoxy (Zhang et al., 1998), though all three material combinations have been investigated (Alderson et al., 2005b). However, the negative Poisson's ratios obtained by this route to date have been small, that is, around v = –0.17 (Herakovich, 1984; Clarke et al., 1994; Zhang et al., 1998). Methods of increasing the value of v have been discussed and these include use of a pre-preg with increased anisotropy (Clarke et al., 1994). In addition to work towards using specially designed software (Evans et al., 2004) to match the mechanical properties of laminates with predicted negative v and prediction of stacking sequences, it has now been possible to specifically maximize the negative Poisson's ratio. It is worthy to note that composites containing novel shaped inclusions such as star-shaped encapsulated inclusion which exhibit auxetic effect can also achieve negative Poisson's ratio (Theocaris and Stavroulakis, 1998).

The other approach to make an auxetic composite is to use auxetic reinforcements. Previously, it was suggested that an auxetic fiber within a composite would resist fiber pullout due to the fiber getting fatter when stretched which results in self-locking into the matrix (Evans, 1990). Alderson et al. (2005c) investigated the composites using auxetic PP fibers as the reinforcement. Single fiber pull-out tests were carried out using auxetic PP fibers embedded in a softened epoxy resin and the self-locking phenomenon was clearly demonstrated. Compared to the positive Poisson's ratio fibers, the auxetic fiber locking mechanism has shown that it is to enable the composite to carry more than twice the maximum load (Figure 12).

Functional composite materials are widely used in sensor and actuator applications. Smith (1994) reported that auxetic polymer matrix is preferred to a non-auxetic matrix for piezoelectric composites consisting of piezoelectric ceramic rods. This is because auxetic matrix converts the compressive planar stress into a compressive longitudinal stress and therefore reinforces the incident vertical compressive stress.

Furthermore, the concomitantly high shear modulus relative to bulk modulus of auxetic polymer matrix enables efficient conversion of incident stresses on the polymer to lateral stresses acting on the ceramic rods, thereby improving the acoustic-to-electrical energy

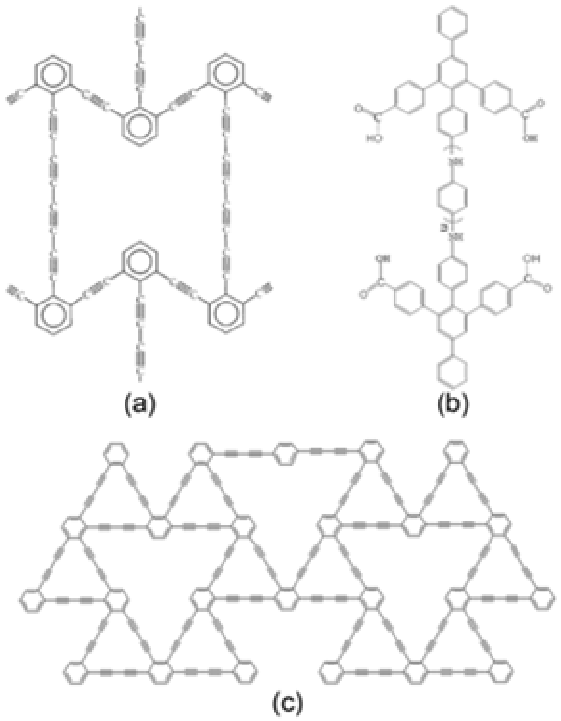

Figure 13. Molecular Structures (a) (1, 4)-refexyne with a negative Poisson's ratio (b) Double-arrow-like molecules (c) Self-expanding polytriangles-2-yne network.
Source: Evans et al., 1991; Wei, 2005; Grima and Evans, 2000b.

conversion.

Molecular-level polymers

Auxetic cellular and microporous polymeric materials have been widely investigated. However, the porosity leads to the lower mechanical properties. It has been suggested that a solid with a porosity of less than 40% cannot be auxetic unless the solid is intrinsically auxetic at the molecular level (Haeri et al., 1992). Needless to say, high porosity may limit many applications because of low strength and structural stability. In order to develop polymeric fibers having high strength and stiffness properties, it will be necessary to produce polymers in which the auxetic effect is derived from microstructures operating at the molecular and nano scales. The design and synthesis of auxetic materials at the molecular level has become one of the most exciting prospects in the development of auxetic materials.

The first attempts at designing auxetic materials at the molecular level were performed for a 2D system of hard cyclic hexamers (Figure 7) (Wojciechowski, 1987) with auxetic behavior being predicted for high densities such that the tangential forces exceeded the normal contact forces between hexamers. Later, most of the works have used the macroscopic re-entrant structure as a template for polymeric molecular design (Evans et al., 1991). By reproducing the re-entrant geometric unit on the molecular scale, two molecular structures such as (n, m)-refexyne (Evans et al., 1991) (Figure 13a) and double-arrow-like molecules (Wei, 2005) (Figure 13b) were proposed. Both structures exhibit auxeticity. Another auxetic molecular structure is self-expanding polytriangles-2-yne network (Figure 13c) developed by Grima and Evans (2000b) according to the rotating unit model (Figure 5). In spite of many theoretical and computational attempts, experimental synthesis of these molecular auxetics has encountered great obstacles due to severe limitation on the yields and solubility of the targeted molecules.

As stated above, one of the successful routes to a molecular level polymer is using liquid crystalline polymer (LCP) model (Figure 9). A series of auxetic LCP were successfully synthesized by He et al. (1998, 2005). One of them is as shown in Figure 14. Besides, dynamic simulations under stress at molecular level were also carried out to predict auxetic polymer behavior (Aldred and Moratti, 2005).

PROPERTIES

Because of negative Poisson's ratio effect, auxetic materials exhibit a series of fascinating properties compared with the conventional materials, such as increased shear modulus(Huang and Blackburn, 2002), indentation resistance (Lakes and Elms, 1993; Alderson, 1999; Smith et al., 1999; Alderson et al., 2000), fracture toughness (Lakes, 1987; Choi and Lakes, 1996), energy absorption (ultrasonic, acoustic, damping) (Scarpa and Smith, 2004; Scarpa et al., 2004a, 2004b), porosity/permeability variation with strain (Alderson et al., 2001; Rasburn et al., 2001; Alderson et al., 2007a), synclastic curvature (Evans, 1990, 1991). Some of these important properties are presented as follows.

Shear properties

Auxetic effect can play in tailoring the mechanical properties of a structure to give enhanced performance. In elastic theory, the material's elastic behavior is expressed by four constants: the Young's modulus (E), the shear modulus (G), the bulk modulus (K) and the Poisson's ratio (v) (Yang et al., 2004). For isotropic materials, the four constants are not independent. They are related by the following equations: $G = E/(2(1+v))$ and $K = E/(3(1-2v))$.

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 v changes, we can alter the values of K and G. For example, when decreasing v to -1, a very high shear modulus relative to the bulk modulus can be obtained. In other words, the material becomes difficult to shear but easy to deform volumetrically (Yang et al., 2004).

Indentation behaviors

Hardness can be increased in an auxetic material due to negative Poisson's ratio. When an object hits an auxetic material and compresses it in one direction, the auxetic material also contracts laterally, that is, material 'flows' into the vicinity of the impact (Evans and Alderson, 2000). This creates an area of denser material, which is resistant to indentation. This phenomenon can thus be explained theoretically. The indentation resistance or hardness of an isotropic material is proportional to $E/(1-v^2)$ when an indenter with a uniform pressure distribution is assumed. As stated above, the variation scopes of v for 3D isotropic materials are from -1 to 0.5. Thus, the $(1-v^2)$ will approach to 0 when v approaches to -1. In this way, for an isotropic material with a given value of E, the indentation resistance increases (towards infinity) with increasingly negative v. As an example, Smith et al. (1999) found that the auxetic foams demonstrated enhanced indentation resistance independent of bulk density and modulus. Their results showed that auxetic foams densify under indentation and the strain field under the indenter is much larger, probably due to enhanced shear

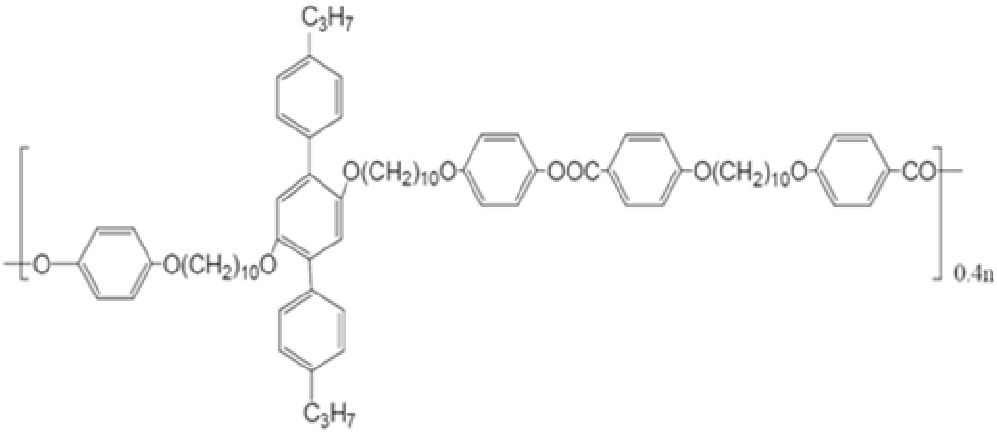

Figure 14. Polymer having laterally attached rods.
Source: He et al., 1998.

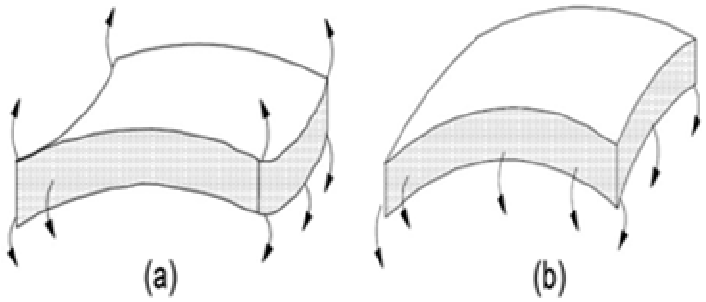

Figure 15. Bending behaviors (a) Curvature behaviors in non-auxetic materials (b) Double curvature-convex shape in auxetic materials. Source: Evans, 1990.

stiffness. Alderson et al. (2000) reported that the indentation resistance of auxetic UHMWPE is enhanced at low loads when compared to conventional UHMWPE.

Fracture toughness

Compared with non-auxetic materials, auxetic materials have increased fracture toughness. The fracture toughness was explored experimentally as a function of permanent volumetric compression ratio, a processing variable (Yang et al., 2004). Compared to that of conventional polyurethane-polyester foam materials, the toughness of auxetic foam is increased by factors of 1.7, 2.1, 2.3, 2.6 and 3.2 with increases of volumetric compression ratio of 2.0, 2.6, 3.2, 3.7and 4.2, respectively (Choi and Lakes, 1992). Auxetic materials also have high crack resistance. If the material has a crack, it expands and closes up the crack when being pulled apart. In other words, this type of material should possess more crack resistance to fracture.

Synclastic curvature

When a conventional material is subjected to an out-of-plane bending moment, the surface is inevitably slightly stretched and leading into shrink the perpendicular direction. It displays anti-clastic curvature due to the edges curl upwards, showing a saddle shape (Figure 15(a)) (Alderson and Alderson, 2007). However, an auxetic material will display synclastic or double curvature as shown in Figure 15(b), producing a dome shape without the need for excessive machining or forcing the material to take up the desired shape which could result in possible damage(Evans, 1990).

Energy absorption

Auxetic materials show overall superiority energy absorption, such as ultrasonic, acoustic and damping, compared to the conventional materials. Scarpa et al. (2004a) reported that auxetic foams could have better sound absorption capacity than conventional foams at low frequencies. The dynamic crushing properties were remarkable in the auxetic foam case, while the conventional foam did not show a significant resilience at high constant strain rate loading (Scarpa et al., 2002).

Variable permeability

Auxetic materials are able to open pores by stretching. This is a useful feature in various types of filtration application. Alderson et al. (2001) first showed how auxetic materials offered improved filter performance from the macro-scale to the nano-scale because of

Table 1. Applications of auxetic polymeric materials.

Areas	Applications
Textiles	Auxetic fibers, threads, functional fabric, color-change straps or fabrics.
Industry	Reinforcement fibers, air filters, gasket, fishnet, rope or cord, filter, fastener, rivets, seal, seat cushions, earphone cushions, shock absorbers, sound absorbers, stress decay, packaging materials, radome.
Aerospace	Curved body part, aircraft nose-cones, wing panel.
Protection	Crash helmet, projectile-resistant or bullet proof vest, shin pad, knee pad, glove, porous barrier, protective clothing, car bumpers.
Biomedical	Bandage, wound pressure pad, dental floss, artificial blood vessel, artificial skin, drug release, surgical sutures, muscle/ligament anchors.
Sensors and actuators	Hydrophone, piezoelectric devices, miniaturized sensors.

their unique pore-opening properties and characteristics. Polymeric auxetic materials and structures can enhance pore size and shape adjustment (Alderson et al., 2001) when pressure increased or subjected to uniaxial stretching. These characteristics can overcome the reduction in filtration efficiency and increased pressure across the filter due to the pores blocked. In addition, the pore size is a function of applied strain which is smart release mechanism (Alderson et al., 2007a).

APPLICATIONS

Auxetic polymeric materials have been identified in a series of applications in textiles, industry, aerospace, protection, biomedical, sensors and other sectors. Generally, applications of auxetic polymeric materials are mainly based on unusual Poisson's ratio, superior toughness, resilience and shear resistance, sound and damping absorption. Some of their main applications are listed in Table 1.

The use of auxetic fabric formed by auxetic filaments or yarns to deliver active agents could lead to intelligent textiles having anti-inflammatory, anti-odour, or drug-release capabilities (Alderson and Alderson, 2005). In addition, the auxetic fabrics can reduce clothing pressure which conduces comfortable. Auxetic fibers are suitable for composite reinforcement due to pullout resistance. Auxetic polymeric materials used in filter systems provide enhanced defouling and pressure compensation properties. Auxetic foams used in seat cushions could reduce pressure-induced discomfort.

The potential exists to develop auxetic materials-based composites and related technologies for aerospace materials and systems having improved performance, such as impact, failure resistance, energy absorption, complex curvatures, structural health monitoring and adaptive and deployable structures (Alderson and Alderson, 2007).

Auxetic polymeric materials are good in combination with other materials for personal protective clothing or equipment such as crash helmet, bullet proof vest, shin pad, knee pad or glove due to wonderful energy absorption properties.

Artificial blood vessel is a typical example for the biomedical application. An auxetic blood vessel will increase in wall thickness in response to a pulse of blood flowing through it, thereby resisting eventual rupture due to wall thinning (Evans and Alderson, 2000). Other potential biomedical applications include surgical implants, suture anchors, muscle/ligament anchors and dental floss. For example, auxetic dental floss offers the ability to expand to fit the widely differing gaps between human teeth and with in-built drug release. Auxetic polymeric materials can advantageously be used in hydrophone, electrodes in piezoelectric sensors and other sensors due to the low bulk modulus making them more sensitive to pressure (Evans and Alderson, 2000). Other new applications of auxetic materials have being explored.

RESULTS AND CONCLUSIONS

Conventional polymeric materials via specific process to achieve auxetic effects can broaden their applications. Auxetic polymeric materials show unique properties, compared to ordinary materials such as enhancement of shear modulus, indentation resistance and fracture toughness. However, auxetic materials normally have lower stiffness due to porous structures. In order to overcome this problem, one of the attracting increasing trends is to develop molecular auxetics. The molecular design incorporating nanotechnology can produce a range of auxetic nanomaterials. In this way, it can be expected to obtain high modulus auxetic materials and these materials having potential application in structure, sensor, molecular sieve, separation and other fields. Furthermore, the auxetic behavior is scale-independent and so the structure that can be used in many other fields. For example, it can obtain auxetic fabrics via proper design of textile structures from either or both auxetic and non-auxetic yarns. Thus, for future work it is necessary to collaborate with researchers from other areas such as textile, mechanics, chemical and biological to explore the potential applications.

ACKNOWLEDGEMENTS

The work described in this paper is supported by a grant from The Research Grants Council of Hong Kong Special Administrative Region Government in the form of a GRF project (Grant No. PolyU 5181/09E).

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