Auxetic Polymers in Textiles - Review
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ABSTRACT: In the past few years, there is an advanced development in manufacturing process in Technical Textiles and this review deals with technology of materials with Poisson’s Ratio. Common Materials have poisson’s ratio ranging from 0.0 to 0.5 but Auxetic material possess Negative Poisson’s Ratio (NPR). In recent years, the use of Auxetic Materials has attracted more and more attention in Textile Industry. As they expand laterally when stretched longitudinally and contract laterally when compressed. This review covers with general information about Auxetic Material, Auxetic Polymers and manufacturing it from Conventional Fibres, Application and Uses.

KEYWORDS: Auxetic Materials, Negative Poisson’s Ratio, Non-woven, Fibers, Auxetic Effect

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1. INTRODUCTION
Auxetic Materials vary from different kinds of Conventional materials as they are depending upon Negative Poisson Ratio (NPR). They have a rubber like Property means as they expand when stretched and get contract when compressed [1]. This kind of behavior gives auxetic materials an various enhanced effect like shear stiffness, increased plane strain fracture toughness, increased indentation resistance and improved energy absorption properties [2,3]. An improved indentation resistance makes them suitable for use in protective equipments; an featured ability to formed doubly curved surfaces particularly to construct dome-shaped surfaces while its acoustic properties make them suitable for making sound proofing equipments [4]. Auxetic behavior achieved from any material level that is from molecular to macroscopic as the Poisson’s ratio is a physical parameter that is independent of any material scale.[5,6]

With a Successful production of auxetic materials leads to the manufacturing of different materials such as polymers, metals, ceramics, composites and a variety of products with negative poisson ratio which were been proposed, investigated and fabricated, including polymeric and metallic foams[7-13], honey combs [14-19].

Use of Auxetic materials varies from industry to industry as they have a lot of potential application from biomedical to automotive and defense industries. Also they have an application in fiber reinforcement as a composite material in Crash helmet, Sports Equipment, Filtration and shock absorbing materials [20]. Generally there are two roots for manufacturing auxetic textiles. The first one includes the use of auxetic fibers to produce an auxetic textile structure, whereas the other utilizes conventional fibers to produce an auxetic textile structure.

2. MECHANISM
2.1 Auxetic Polymers
The first synthetic auxetic microporous polymer was anisotropic form of expanded polytetrafluoroethylene (PTFE). Caddock and Evans [21] and Evans and Caddock [22] found that a large negative strain-dependent Poisson’s ratio, with values as large as -12, was a consequence of the polymer’s complex microstructure and not an intrinsic property of the PTFE itself. Nodules interconnected by fibrils of approximately 1 μm diameter react to applied force by hinging the fibrils and cooperatively producing an auxetic effect. Once the fibril hinging is complete, the additional stage of fibril stretching was proposed as an explanation of the experimental data on tensile loading at higher strains for auxetic PTFE. [23,24]

Different attempts were made to reproduce that microstructure and to achieve auxetic behavior in other polymers. Alderson and Evans [26] presented a similar microstructure of a microporous form of ultra high molecular weight polyethylene (UHMWPE) produced by a novel thermoforming processing route. These polymers demonstrate Poisson’s ratios as low as ~1.2, depending on the degree of anisotropy in the material. A similar three-stage thermal processing route was used to engineer polypropylene [27] and nylon [24] also consisting of nodules interconnected by fibrils. The polymers were processed by compacting finely divided powder with a rough surface, sintering, and extruding the powder through a conical die. Examination of powder morphology on the auxetic behavior revealed that particle shape, size, and surface roughness are critical variables for successful processing. The negative Poisson’s ratio values for this polypropylene were up to ~0.22 at 1.6% strain.[27] Alderson et al.[28]reported the fabrication of a highly fibrillar auxetic form of UHMWPE, utilizing a powder processing route comprising only two stages: sintering and extrusion. The density, flexural modulus and flexural strength of the UHMWPE were substantially reduced due to the omission of the compaction stage that usually occurs prior to sintering and extrusion. However, attenuation absorption for this two-stage material excelled that seen for either the structural (i.e. with a modulus of at least 0.1 GPa and produced in a three stage process) auxetic material or the conventionally processed UHMWPE. Therefore it is likely to be an ideal material for...
use in energy absorption applications. The extrudates were produced in the form of cylindrical rods. Despite the auxeticity there are limitations in the production of cylindrical auxetic materials (diameters varying between 8 and 15 mm) on a large scale, since the fabrication process is not continuous, therefore restricting it to the laboratory [29, 30].

3. Auxetic textile structures made from Conventional fibres

A way to overcome the disadvantages of producing auxetic materials, which includes a post-processing stage or processing by non-traditional methods, with each step providing additional costs, is to produce auxetic textiles with conventional yarns, as defined by Alderson [31]. Hook [32] presented an auxetic multifilament construction consisting of a high-stiffness filament helically wrapped around a thicker, low-stiffness entirely different filament, with neither of these two constituents required to be auxetic. Upon longitudinal stretching, the high stiff filament straightens and causes the lower stiff filament to helically wrap around it. Such multifilament construction exhibits auxetic behaviour and can be fabricated on existing textile machinery, such as warp spinning. Sloan et al [33] showed that the starting wrap angle of the helical auxetic yarn (HAY) has the greatest effect on auxetic behavior as regards both the magnitude and the strain range over which it appears. Other parameters which influence auxetic performance are the diameter ratio of wrap to core fibers and the fibers' inherent Poisson's ratio.

They reported the characterization of the helical auxetic yarn with a focus on stiffer yarns, suitable for higher modulus applications such as composites and blast mitigation. Wright et al [34] reported on the manufacture and characterization of different HAYs and fabrics with low stiffness or tensile modulus. The auxetic effect of HAY is present in real-world strain regimes. Therefore, these yarns and fabrics are suitable for healthcare, particularly bandages, compression hosiery and dynamic stiffness support garments, as well as fashion apparel. The HAY is especially well suited to woven fabrics, even though knitting is also feasible. The manufactured plain weave narrow fabric exhibited a thickening of the fabric and thus an out-of-plane negative Poisson's ratio. Shanahan et al [35] also considered auxetic effect in the thickness of fabric. They reported on the theoretical auxetic behavior present in the fabric's effective thickness, as a consequence of the geometrical effect of woven structure and modulus of yarns. Miller et al [36] produced helical auxetic yarns and further used them in a simple weave pattern to fabricate an auxetic textile. Woven textile structure was then used to manufacture a low modulus auxetic composite. The first reported composite to exhibit auxetic behaviour using inherently auxetic yarns was produced using standard manufacturing techniques. As presented with examples above, combining two or more multifilament constructions in an appropriate manner enables the production of auxetic structures. Similarly, Hook [32] patented the woven porous fabric in warp arrangement comprising an array of pairs of adjacent helical auxetic yarns with mirror placement of helices. The weft fibers interconnecting warp yarns may be auxetic or nonauxetic.

Helical auxetic yarns that provide a net increase in the effective diameter of the composite yarn under strain, thereby exhibiting pore-opening effect, when incorporated into fabrics are suitable for different applications. One such case are fabrics that change color and can be used for indicative or aesthetic purposes. These fabrics comprise a basic fabric of different color than the overlaid porous material made from auxetic fibers. Such an arrangement enables color change under an application of strain. This has potential in fashion and other fields where an accurate indication of the suitable tension is required [32]. Pore-opening is also applicable in filtration, where intentional scaling of tensile or compressive load application serves as a tool to vary the pore size in order to control the filtration process [32, 37]. Hook [32] also presented a sample of these fibers made into a porous material that was then used to disperse blast energies from an explosion. The porous material, comprising a plurality of layers, enabled energy from the explosion to be efficiently dispersed through layers and voids between them to mitigate the blast effect. The third possible area of application includes release capabilities, such as garments containing anti-perspirant in the pores of the material, which is released upon stretching the garment and pore-opening [31]. Other possible substances stored in the porous material include antibacterial, antifungal, antiviral, antiyeast or antiamoebic agents, different additives for use in dental floss [31]; applications also include drug delivery and exudate removal, for instance [34].
In comparison to the patent by Hook [32] described a flat textile structure constructed from two-unit composite yarn, Hook et al.[38,39] presented composite materials and structures exhibiting negative Poisson’s ratio, constructed from similarly comprised units made up of two components, with an additional core element in the minimum repeat unit. The core element should preferably be auxetic. The structure may also include matrix components, which are preferably in contact with all the other composite components and may amplify auxetic effect of the material. As the authors claim, the auxetic material is relatively easy to fabricate, is consistent in its structure and properties, has a significant (the system could have a Poisson’s ratio of between 0 and –5) and controllable auxetic effect, and it can also be used to develop complex and useful forms. The structure is appropriate for impact and acoustic absorption applications.

Structures visually similar to the one presented by Hook [32] were reported to be auxetic as a result of other external factor besides the usual, namely a pseudo tensile force created by wetting. Lee et al [40] described making auxetic fibers consisting of two components, of which one is moisture sensitive filament, i.e. it shrinks when it is in contact with moisture. Therefore an auxetic effect can be caused when the fiber is simultaneously exposed to external strain and moisture, or the auxetic effect can be caused by one of these two factors alone.

An array of auxetic fibers is comprised of a woven structure in the same way as presented by Hook32, where a pair of adjacent fibers is of opposite handidness regarding the helices. Ge and Hu [41] recently reported an innovative three dimensional nonwoven fabric structure with negative Poisson’s ratio for composite reinforcement. The structure was made by combining both non-woven and knitting technologies. Four fabric samples with different warp yarn diameters were first manufactured manually. Then their Poisson’s ratio values, under compression along the direction of fabric thickness, were experimentally evaluated. A geometrical model was proposed for the theoretical calculation of Poisson’s ratio values of these fabrics and was compared with experimental data. There was good agreement between the calculated and experimental data.

The results showed that all 3D fabrics displayed auxetic effect under compression, resulting in a unique feature that allows the structure to concentrate itself under the compressive load to better resist the load. This special feature makes this innovative 3D fabric structure very attractive for many potential applications in the automobile industry, the aerospace industry, and in defense and sports equipment, where impact protection can be a highly desirable property.

Figure 2 Helical Auxetic Yarn [33]

Figure 3 Three-dimensional (3D) NPR textile structure: (a) initial state (b) Under Compression
4. AUXETIC FIBRES

Alderson et al [42] were the first to successfully produce auxetic fibers. They developed a kind of auxetic polypropylene (PP) fiber by employing a novel thermal processing technique, based on modified conventional melt spinning technique. This enabled a continuous fabrication process of auxetic polypropylene (PP) fibers. They used a laboratory scale melt extruder in place of a benchtop extruder and a flat profile of 159 °C across all zones of the extruder.26 Even though aligning the molecules, as a consequence of drawing, gives fibers their high modulus, drawing the auxetic fibers causes a loss of the auxetic property. Ravirala et al [45] reported that the main approach for the production of auxetic fibers lies in maintaining the minimum draw ratio.

Due to the relatively low modulus of auxetic fibers, Simkins et al [43] considered the possibilities to increase it to avoid the problematic post processing of fibers on conventional textile equipment. They annealed fibers at various times and temperatures. Annealing enhanced the mechanical properties of these fibers, it increased the modulus; the tensile strength was at least 1.5 times higher in comparison to the un-annealed fibers. [45] and the fibers were more uniformly auxetic. The developed fabrication process of polypropylene fibers is flexible enough to be used for the production of other polymeric fibers with the ability to achieve auxetic behaviour. The same partial melt extrusion technique was used to produce auxetic fibers from polyester and nylon [46]. Ravirala and co-workers [46] produced auxetic polyester fibers. They observed that the key processing parameter was extrusion temperature which played a critical role in attaining the auxetic effect. The auxeticity of the polyester fibers increased considerably in the fibers fabricated at a processing temperature of 225 °C, in comparison to fibers fabricated at 220 °C. It was found that the auxetic effect occurs over an extremely narrow temperature window [47]. This applies also to polypropylene and nylon fibers. This thermal processing technique seems to result in lower modulus fibers which cannot be drawn to improve mechanical properties. Heat treatment improved the properties (strength) just enough to allow textile production, while limiting its overall effect. The reason for this kind of behaviour lies in the microstructure of the fibers. Kim L. Alderson [26] concludes that larger scale auxetic polymers such as cylindrical rods appear to have a different causal mechanism to auxetic fibers. Extensive microscopy of the fibers revealed no evidence of the expected nodule-fibril microstructure [47]. Figure 4 shows the microstructure of an interlocked particle model, which seems to have a granular structure that consists of powder particles “glued” together exclusively by surface melting [26] and a low porosity. Alderson et al. [47] explained the possible causal mechanism for auxetic behaviour in this system based on a closely packed rough particle assembly, where particles undergo surface melting, which results in the formation of a network of connected interlocking rough particles. Besides the barrel temperature, which has the main role in processing the appropriate connected microstructure of auxetic fibers, the differential ratio of surface-melted thickness to particle diameter is another important factor. The mechanical properties of these auxetic fibres are a consequence of a structure and deformation mechanisms at the micro scale. Consequently the stiffness and strength are not comparable to corresponding conventional fibers, extruded from a fully molten polymer, where mechanical properties arise due to structure and deformations at a molecular level [48].

Team of researchers at the University of Bolton have used the auxetic fibers produced by a partial melt spinning process and integrated them into prototype fabrics, both knitted and woven. The results have not yet been published [26]. To increase the modulus of auxetic fibers for use in textile structures without additional fiber treatments, fibers will have to be produced in a different manner. One theoretical proposal was made by Evans et al [1] presented molecular level auxetic polymer. Polyphenylacetylene single crystalline network based on the auxetic re-entrant honeycomb structure was already proposed and analysed by Abd El-Sayed et al [49] and Gibson et al [14]. Evans et al. [1] employed a general approach in designing molecular auxetics, namely the downscaling technique of known auxetic macro structures to the molecular level [50]. Although auxetic behaviour, which is assumed to arise from concurrent stretching, hinging and flexing of the sarms of this molecular network under tension, was predicted in one plane, the structure was too heavily crosslinked to be physically possible. The flexyne/reflexyne networks model by Evans and co-workers [1] was further developed by Wei [51], who proposed a self assembled copolymer having a double-arrow-like sharpblock and a spring-like soft segment. A hydrogen-bonded polymer network is more realizable with auxetic property predicted in the plane of the structure.

Molecular auxetics consisting of open, hinged networks from molecular building blocks have also been proposed by Gardner et al [52], based on low-barrier rotational changes that would result in polymorphic molecular solids having significantly different volumes under strain. Wojciechowski [53] proposed a two-dimensional nonchiral model of tri-atomic molecules. The cyclic trimers form a mechanically stable and elastically isotropic auxetic phase based on modeling considerations. Grima and Evans [54] suggested a series of self expanding polyphenyl acetylene molecular networks consisting of connected rotating triangles as a potential molecular deformation mechanism for auxetic behaviour, also named cooperative rotation of the corner-sharing triangles. Grima et al. [55] predicted auxetic networked polymers based on calyx [4] are molecular building blocks, which are not as easily realized. Baughman and Galvao [56] discussed twisted-chain structures in polymeric materials, where the auxetic property is the result of a mechanism called the change in twist of helical chains. Another approach being one of the most simple and promising approaches in the endeavour to produce synthetic molecular-level auxetic polymer was predicted by He et al. [57,58], who described a system that was more easily reproducible, based on liquid crystalline polymers (LCPs). The LCP is composed of chains of rigid rod
molecules transversely or longitudinally connected to flexible spacer groups. The laterally attached rigid rods in the quiescent or un-stretched state orient parallel to the terminally attached rigid rods. However, when the system is stretched, the laterally attached rigid rods change their position. This site-connectivity driven rigid rod reorientation causes an increase in the inter-chain distance, which resembles the nodule-fibril mechanism. Thus far such materials with negative Poisson's ratio have not been created.38

5. APPLICATION & USES

Currently the uses for auxetics are limited, and in those applications they are probably not knowingly used for the auxetic effect itself. Examples include pyrolytic graphite for thermal protection in aerospace applications, large single crystals of Ni Al in vanes for aircraft gas turbine engines, and an expanded form of PTFE used to make Goretex. However, the development of new auxetic materials and processing routes in recent years has been accompanied by a number of patent applications and publications from organizations including Toyota, Yamaha, Mitsubishi, AlliedSignal Inc, BNFL and the US Office of Naval Research, all relating to the emerging potential of these materials.

5.1 Biomedical Industry

Key areas of application are seen in the biomedical field. Prosthetic materials, surgical implants, suture/muscle/ligament anchors and a dilator to open up blood vessels during heart surgery are all possible. Another area relates to the use of auxetic materials in piezoelectric sensors and actuators. Auxetic metals could be used as electrodes sandwiching a piezoelectric polymer, or piezoelectric ceramic rods could be embedded within an auxetic polymer matrix. These are expected to increase piezoelectric device sensitivity by at least a factor of two, and possibly by ten or a hundred times. The development of auxetic materials for micro and nano mechanical and electromechanical devices is also being investigated.

5.2 Filters

Auxetic foam and honeycomb filters offer enhanced potential for cleaning fouled filters, for tuning the filter effective pore size and shape, and for compensating for the effects of pressure buildup due to fouling.
benefits rely on the pores opening up both along and transverse to the direction of a tensile load applied to an auxetic filter. The pores of a non-auxetic filter open up in the stretching direction but close up in the lateral direction, leading to poorer filter performance, figure 5. However, stretching an auxetic filter improves performance by opening pores in both directions. The effect of stretching on the defouling of an auxetic polymeric honeycomb fouled with glass beads has been investigated. For the particular honeycomb studied the value of $v$ is dependent on the stretching direction. The studies clearly demonstrate that defouling is enhanced when the filter is loaded in the direction with the largest negative $v$.

![Figure 5 Schematic of particulate defouling capabilities non-auxetic and auxetic materials](image1)

Figure 5 Schematic of particulate defouling capabilities non-auxetic and auxetic materials

![Figure 6 Fibre Pullout in composites](image2)

Figure 6 Fibre Pullout in composites

![Figure 7 X-ray tomographs of the converted PU foam](image3)

Figure 7 X-ray tomographs of the converted PU foam

5.3 Auxetic Fibre Reinforced Composites

Auxetic fibre reinforcements should also enhance the failure properties of composites. Fibre pullout is a major failure mechanism in composites. A unidirectional composite loaded in tension will undergo lateral contraction of both the matrix and fibre materials, leading to failure at the fibre/matrix interface. Auxetic fibres on the other hand allow the possibility of maintaining the interface by careful matching of the Poisson’s ratios of the matrix and fibre, Figure 6 [58].

6. RECENT DEVELOPMENTS IN AUXETIC POLYMERS

6.1 Piezomorphic Pu Foam

Large strain deformation is necessary to produce an elastic-gradient material. In recent developments in auxetic polymers, the elastic response of a material is
undergone large strain deformation [59] through tailored Young’s modulus and Poisson’s ratio to control morphing behavior. Through X-ray tomography images, it showed a transition region from an initially thick to a thin cross section of the converted and unconverted foam, as illustrated in Figure 7. It reported that the auxetic effect, as shown in the bottom of the image, is due to the higher density re-entrant foam.

7. FUTURE APPLICATIONS

Despite the very significant developments to date we have only scratched the surface of this exciting and multidisciplinary field. The successful synthesis and development of molecular and multifunctional auxetics represent key opportunities for the future. In addition to leading to materials with extreme properties such as high modulus and strength, these advanced materials will have potential in sensor, drug release and separations applications. By accepting a negative Poisson’s ratio as a positive property we are truly expanding the applications of these fascinating materials.

8. CONCLUSION

Extensive recent investigations of textile structures exhibiting auxetic potential and performance properties of the analysed auxetic materials indicate that there will be further development of auxetic polymers and auxetic fibers. The auxetic potential of the textile structures made from conventional raw materials has become the interest of many researchers. As the knitting technology enables the design of various mesh planar structures and foldable 3D structures with auxetic potential, this research field has greatly expanded. On the other hand, 3D foldable weft knitted structures with auxetic potential can also be an inspiration for fashionable knitwear with an unconventional visual effect. For this reason, all developed knitted structures with auxetic potential have also been analyzed from the artistic-aesthetic point of view.

REFERENCES

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