Progress in auxetic fibres and textiles

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Abstract Auxetic materials are those which expand when stretched and contract when pushed. One area which is currently attracting attention is in the production of auxetic fibres and textiles. Here, the history of auxetic microporous polymers and subsequent fibres development and production is reviewed along with attempts to understand how the auxetic effect is achieved based on the observed microstructures. Larger scale auxetic polymers appear to have a different causal mechanism to auxetic fibres. A natural development from the production of auxetic fibres is to use the fibres to produce textiles. Progress in this area is examined together with work towards using conventional fibres to produce a textile which is auxetic due to its structure rather than its constituents. Possible applications are also presented.

Keywords **Auxetic fibres, textiles, negative Poisson's ratio, microstructure.**

Résumé **Les avancées dans les fibres auxétiques et les textiles**
Les matériaux auxétiques s'expandent à l'étirement et se contractent à la poussée. La production de fibres et textiles auxétiques est un domaine qui attire actuellement l'attention. Après un rappel historique, cet article présente le développement et la production des polymères microporeux auxétiques, ainsi que les études visant à comprendre l'effet auxétique, par l'observation des microstructures. Il apparaît que les polymères auxétiques de plus grandes échelles présentent un mécanisme différent de celui des fibres auxétiques. L'un des développements naturels des fibres auxétiques est la production de textiles. Les progrès dans ce domaine sont présentés, de même que les travaux en vue de l'utilisation de fibres classiques pour produire un textile qui soit auxétique du fait de sa structure, et non de ses constituants. Les applications possibles sont également présentées.

Mots-clés **Fibres auxétique, textiles, ratio de Poisson négatif, microstructure.**

Auxetic materials have the unique property of increasing in thickness when pulled when compared to an elastic band, which gets thinner when stretched [1]. This is because the Poisson's ratio of the material, ν, is negative. This property is shared by a range of materials, from certain types of skin and bone to forms of silica and can be engineered into foams and polymers, among others [2]. This article will concentrate on one of the most interesting areas of current research: the production and deployment of auxetic polymeric fibres and developments in the area of auxetic textiles.

However, the initial work on auxetic polymers did not begin with fibres, but rather with the production, characterisation and testing of polymer cylinders by the powder processing techniques of compaction, sintering and extrusion. Following the discovery, by Evans and Caddock in 1989, of an expanded microporous form of polytetrafluoroethylene (PTFE) which did indeed expand when stretched, work began at the University of Liverpool to reproduce this behaviour in other polymers. A detailed investigation of the microstructure of PTFE was undertaken [3] and it was found to consist of nodules interconnected by fibrils, as shown in *figure 1*. *Figure 2*

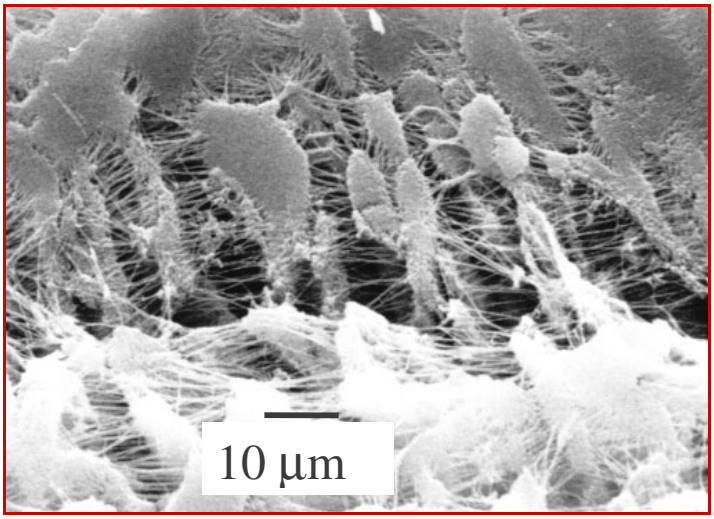

Figure 1 - Microstructure of auxetic polytetrafluoroethylene showing nodules interconnected by fibrils.

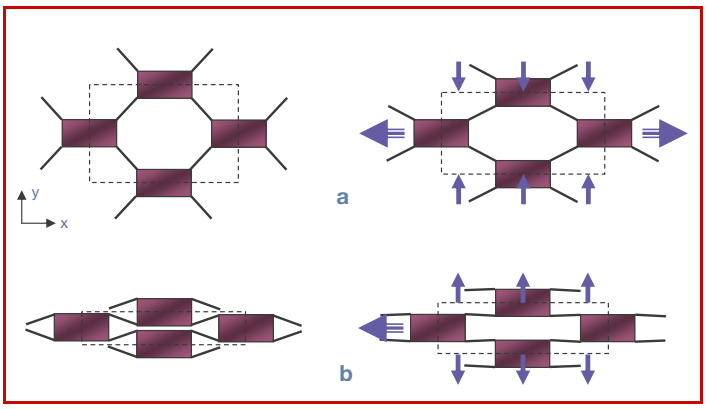

Figure 2 - Schematic showing how the nodule fibril microstructure allows a negative Poisson's ratio. (a) shows a conventional material and (b) an auxetic material.

illustrates schematically how the structure leads to the auxetic effect, with the fibrils acting as hinges to cause the nodules to translate. The first new polymer to be manufactured to achieve a nodule-fibril microstructure was ultra high molecular weight polyethylene (UHMWPE) [4]. The processing route found to be necessary to achieve the nodule-fibril microstructure was based on the partial or surface melting of the polymer powder particles in a bench-top extruder. The compaction stage was found to be required only to adjust the structural integrity of the extrudate, with partial sintering being the most important stage in processing. For UHMWPE, a sintering time of 20 min at a temperature of 160°C was required and Poisson's ratio values as low as - 6 were obtained, but for very low structural integrity samples. The next stage in this work was to transfer the skills used in the manufacturing of UHMWPE to other polymers and this was successfully tried and achieved for a further two polymers, polypropylene (PP) [5] and nylon [6]. PP was used as a basis to examine the effects of powder morphology on processability and this established the need for a finely divided powder with an average particle size distribution between 50 and 300 µm in conjunction with a rough particle surface. The processing conditions for PP include the key sintering temperature of 159°C and time of 20 min, and the resulting extrudates had Poisson's ratio values as low as - 0.22 with good structural integrity. This is much less than for UHMWPE, and is due to the microstructure which in PP has far fewer fibrils interconnecting the nodules. The microstructures for both UHMWPE and PP are shown in *figure 3*.

The cylinders produced are useful for performing simple tests to determine properties, but are difficult to deploy in any useful applications. The applications can stem from the actual property of expanding when stretched (such as in sealants) or can be based on property enhancements predicted as a consequence of the negative Poisson's ratio. For example, the hardness of a material, H, is related to ν as:

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

where x is a constant depending on the analysis used, *e.g.* for classical Hertzian indentation, x = 2/3. What this equation says is that if ν = - 1, then the material would be infinitely hard. This would also be true if ν = + 1. However, for an isotropic material, ν can only range from - 1 to + 1/2, so any value between - 1/2 and - 1 should result in enhancements. As well as indentation resistance, other properties predicted to be similarly enhanced include fracture toughness, shear modulus and energy absorption [2].

With these predicted benefits in mind, producing forms of auxetic polymers which can easily be deployed has driven the research towards the production of auxetic fibres.

Auxetic fibres

Auxetic fibres were first produced in 2000 at the University of Bolton by Simkins and Alderson [7]. A short research project funded by the Nuffield Foundation allowed the very early stages of this work, concentrating initially on PP. The idea here was to take the processing route developed for the cylinders as a basis for fibre production. In place of a benchtop extruder, a laboratory scale melt extruder was employed, but the key parameter of 159°C as the processing temperature was retained. The melt extruder has five separate zones, all of which can be individually temperature controlled, and for conventional processing, it is usual to use a temperature profile. For the production of auxetic fibres, however, a flat 159°C across all regions of the

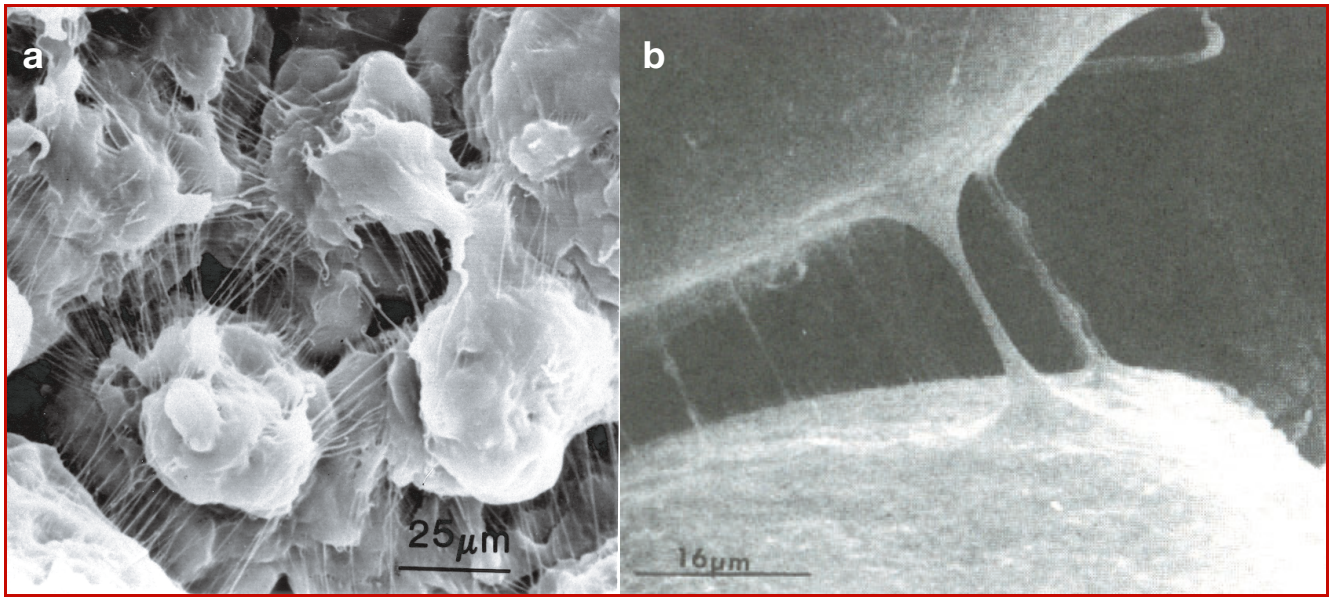

Figure 3 - Microstructures of auxetic (a) ultra high molecular weight polyethylene and (b) polypropylene.

extruder is necessary. A further difference in production of auxetic fibres is that the extruder is run at a relatively low speed. This is to take account of the 20 minutes sintering time in the cylinder manufacturing route. The screw speed used is 1.047 rads^{-1}, resulting in a throughput of 6 g/min.

In conventional fibre production, as the fibre emerges from the spinneret, it is drawn and this aligning of the molecules gives fibres their high modulus. However, a detailed investigation here revealed that drawing of the auxetic fibres causes a loss of the auxetic property. So, the fibres are collected at a take up speed of 0.03 ms^{-1} and wound straight onto bobbins. The resulting fibres have a modulus of 1.3 GPa. 40% of the fibres produced are auxetic with typically 20% of their length displaying auxeticity. This may seem to be a small fraction but the auxetic sections display a Poisson's ratio of ν = - 1.62, which results in the overall fibre having a Poisson's ratio, ν = - 0.60 ± 0.05.

Initial attempts of post processing the fibres on conventional textile equipment were problematic due to the relatively low modulus. So, possible solutions to increase the modulus were considered. As a first attempt, the fibres were annealed at a variety of times and temperatures [8]. The results of this were very positive, with a number of conditions obtained which not only retained auxeticity, but also increased the modulus. For example, annealing at a temperature of 110ºC for just 5 min increased the modulus to 1.8 GPa. The Poisson's ratio in this case was negative for 40% of the fibres tested, and of these, 70% of the length was auxetic with an average ν = - 1.30, *i.e.* the fibres were more uniformly auxetic. This increase in modulus does allow for some textile production which will be discussed later, but the modulus is still very low, with the best achieved, with auxeticity being retained, 2.3 GPa. This was obtained using an annealing temperature of 160ºC and a time of 5 min. Alternative strategies are thus required, with the manufacture of other polymers by this route being the first attempted.

Using the same partial melt extrusion technique, auxetic fibres were produced from both polyester and nylon [9]. The polyester fibres were produced at a flat temperature of 225ºC, with a screw speed of 0.525 rads^{-1}, a take up speed of 0.075 ms^{-1} and no drawing. This produced a fibre with an average Poisson's ratio, ν = - 0.70, but with a low modulus of 1 GPa. For the case of the nylon fibres, the manufacturing specification is once again a flat temperature of 195ºC in all zones of the extruder, with a screw speed of 1.05 rads^{-1}, a take up speed of 0.03 ms^{-1} and no drawing. The resulting fibre had an average Poisson's ratio, ν = - 0.17, but with an even lower modulus of 0.5 GPa.

It appears that in producing an auxetic fibre by this technique, the result is always a lower modulus fibre which cannot be drawn to improve mechanical properties. Heat treatment has a limited effect, improving the strength just enough to allow textile production.

The key to understanding why this is the case comes with examining the microstructure of the fibres. Initially it was believed that the fibres would have a nodule-fibril microstructure albeit with a vastly reduced number of nodules interconnected by fibrils. However, extensive microscopy of the fibres has failed to find evidence of this type of structure. The most indepth study was carried out by Simkins and she used liquid nitrogen to "freeze" the fibres before sectioning, revealing the microstructure seen in *figure 4*. This shows that the fibre appears to have a granular structure consisting of the powder particles "glued" together by surface melting only [10]. There is very little porosity and

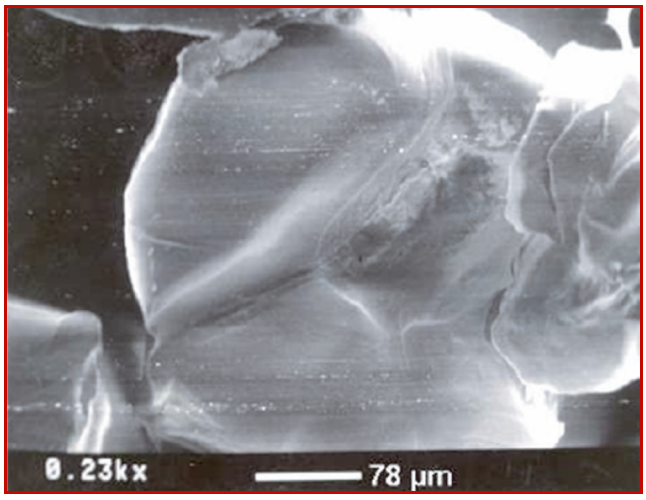

Figure 4 - Microstructure of an auxetic polypropylene fibre showing its granular nature.

the core of the powder particles appears to remain largely unmelted and thus can be assumed to be amorphous. So, rather than a nodule-fibril model to explain this behaviour, there needs to be an understanding based on a closely packed rough particle assembly. Taking as a basis interlocking rigid hexagons, an analytical rough particle model was developed by Ravirala *et al.* [10]. This is close to the microstructure and in addition is also based on existing theoretical models for auxetic behaviour, notably Wojciechowski's 2D rough disc assemblies and hard cyclic trimers [11]. An example of this type of structure already in existence is, surprisingly, found in the Tokai nuclear reactors developed in the 1950s [2]. Here, an interconnected structure is formed by, effectively, rectangular keys (male) and geometrically matched keyways (female) on alternative faces of each hexagon. The auxetic effect is produced by translation of the hexagons with respect to each other.

It is recognised that to obtain order of magnitude increases in the fibre modulus, there needs to be a very different approach, namely to work at the molecular level. First attempts at producing auxetic polymers at the molecular level were theoretical and used as a basis the macroscopic re-entrant honeycomb structure. This did predict auxetic behaviour but for wholly unrealistic structures which were too heavily crosslinked to be physically possible [1]. Looking at the same problem from a different angle, Anselm Griffin at the American Georgia Institute of Technology has predicted auxetic behaviour in a more easily realised system, based on liquid crystalline polymers (LCPs) [12]. This is shown schematically in *figure 5*. The LCP consists of chains of rigid rod molecules connected by flexible space groups, which attach to the ends of some of the rods and to the sides of others. The mechanism for auxetic behaviour bears a resemblance to that of the nodule-fibril mechanism in that it is based on rotation of the rods attached to the sides, which causes an increase in the interchain separation, when the system is stretched. Work towards the synthesis of this system is currently underway.

Auxetic textiles

One area in which there is a considerable amount of work currently ongoing is to produce auxetic textiles. Applications which are envisaged include using the auxetic property, *e.g.* as a bandage for compression therapy, where the bandage

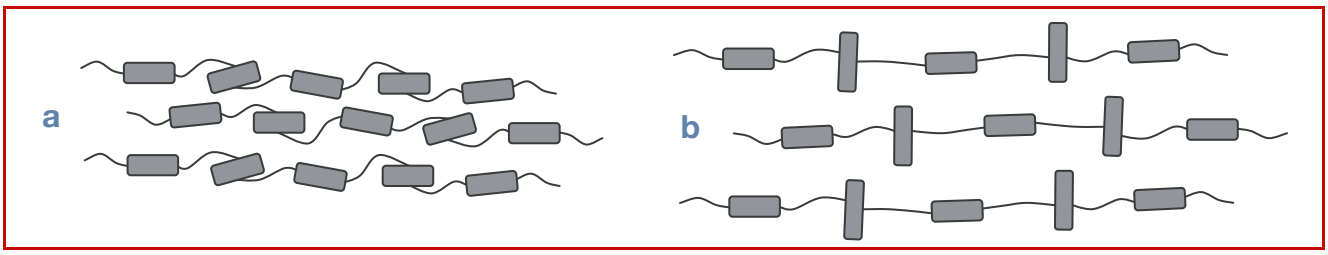

Figure 5 - Theoretical LCP in (a) undeformed and (b) deformed state due to horizontal stretching.

would compress swelling of the limb and improve breathability, and exploiting the auxetic benefits. Examples of the latter include using the double curvature characteristic of an auxetic material, which would improve comfort and fit for the wearer, and targeting the energy absorption characteristics for development of protective and sports clothing, like cricket pads, bulletproof vests and blast curtains. Two approaches can be considered: using auxetic fibres to produce a textile or using conventional fibres to produce an auxetic textile structure.

The first approach has been investigated by two main groups. Evans and Hook at the University of Exeter have produced an auxetic multifilament construction which consists of a high-stiffness filament wrapped helically around a thinner, low-stiffness filament, with neither of these two constituents being required to be itself auxetic. When the multifilament is stretched, the high stiffness filament straightens, causing the lower stiffness filament to helically wrap around it [13]. Examples of the materials used include an aramid-nylon yarn. The multifilaments are now being deployed in fabrics for protective blast curtains. The University of Bolton have taken the auxetic fibres produced by partial melt spinning and processed these to obtain prototype fabrics. Initially, the fibres were annealed as described above and knitted on a simple hand knitting machine. This has been further developed by Uzun, working with Alderson and Alderson at the University of Bolton [14]. He produced both plain knitted fabrics and simple plain weave prototype fabrics. Before knitting, the fibres were cured with lubricant for 4 hours to enable their use on a Flat V-Bed knitting machine. *Figure 6* shows an example of the prototype fabric produced. A series of tests to study the abrasive resistance of the knitted fabrics have recently been undertaken with the results, currently being analysed, appearing to be extremely positive.

The second approach to produce an auxetic textile is to use conventional fibres (though using auxetic ones is also possible) and to knit them into an auxetic structure. There have been three reported methods of achieving this aim. Ugbolue and co-workers reported in 2008 an auxetic knit structure produced from Nomex and polyester yarns. The wales are knitted from open lap loops using thicker low stiffness filaments. A high stiffness filament is inlaid around aramid loops as underlaps. This fillet warp knit fabric is auxetic, especially at the first stage of stretching, with ν =- 0.5 [15]. Hu *et al.* have recently reported an auxetic weft knit structure fabricated on a computerised flat-knitting machine. They report that the auxetic effect decreases with increased strain in the course direction and that the main structure parameter affecting auxeticity is the opening angle of the initial structure [16].

Here at the University of Bolton, work has concentrated on an auxetic warp knit structure with a patent filed initially in 2006 [17] followed by a second more detailed patent in 2010 [18]. The design process began with a review of known auxetic structures and mechanisms together with advice from knitting experts. Based on this, the topology selected was taken from the work of Sigmund *et al.* [19]. This was a double arrowhead or triangular structure, with the auxetic effect produced by hinging leading to opening of the arrowheads. The first fabrics produced used Dorlasten and two different diameter polyester monofilaments. The auxetic effect was measured on heat set fabrics at - 45° and + 45° to the warp direction, with Poisson's ratio values of up to ν = - 0.22. Work on this design is continuing.

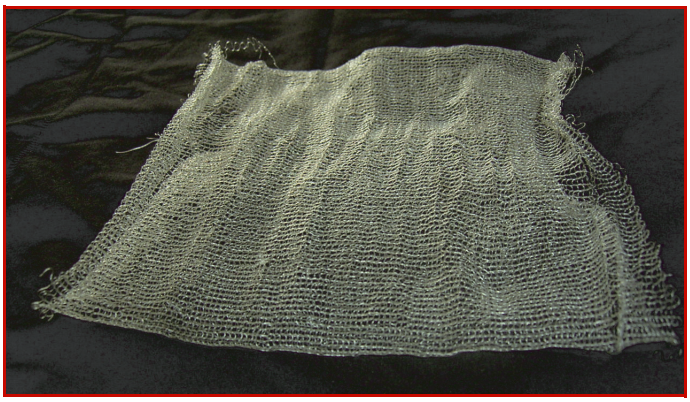

Figure 6 - Textile knitted from auxetic fibres.

Conclusion

This review has examined the state of the art in an exciting and fast moving area of fibres and textiles research. Progress is being reported by a number of groups in the production of auxetic fibres and textiles with several different approaches being considered. Fibre production is limited at the present time to multifilament constructions or relatively low modulus melt extruded fibres. The ultimate aim is to produce a molecular level auxetic fibre to ensure a high modulus and work towards this is reported here. Nevertheless, this is a vibrant area of work driven by a variety of applications from blast curtains to compression therapy bandages.

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