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On the effect of heat and solvent exposure on the microstructure properties of auxetic foams: A preliminary study

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The effect of elevated temperature and solvent exposure on the microstructure of auxetic polyurethane foams is investigated. It is shown that such effects result in an expansion of the auxetic foams accompanied by the removal of the highly convoluted features in the microstructure of auxetic foams with the result that such foams lose their auxetic characteristics. It is also shown that such changes do not occur if the foams are subjected to the high temperature or solvent exposure in a contained state which does not permit the expansion. This means that auxetic foams can still be used in such environments provided that the right precautions are taken (e.g. putting them in a cover thereby constraining them to retain their volume).

1 Introduction Auxetic materials exhibit the unusual property of becoming fatter when uniaxially loaded as opposed to most common materials which contract under such loading conditions. This property is reflected in the Poisson's ratio of the material, a dimensionless property defined as the negative of the ratio of the lateral and longitudinal strains. Thus, conventional materials are characterized by a positive Poisson's ratio while auxetic materials are characterized by a negative one [1–57]. This property occurs at different length scales including the nano [2, 4–21], micro [1, 22–44] and macro[45–57] levels and can be found in naturally occurring materials, for example, in certain metals [10] and minerals [11–17, 18–21] or can be introduced deliberately into a system, for example in foams and micro-porous polymers [22–44].

It is also known that this property gives rise to various enhanced properties such as increased indentation resistance [3, 22], the ability to form dome shaped surfaces [1–3] and enhanced sound and vibration absorption properties [28–30]. Owing to such benefits there has been a substantial amount of research in this field, accompanied by significant progress particularly in areas related to auxetic foams in view of their many applications which include sandwich panels, automotive components, filters, packaging, cushioning, protective clothing and energy absorbing applications.

The first auxetic foam was made from conventional foam through a heating/compressing process, discovered by Lakes [1]. This method involves compressing the conventional foam triaxially by a volumetric compression factor in the range between 1.4 and 4 at a temperature slightly above the softening temperature of the foam material. Various modifications to this method were also investigated. In particular, a manufacturing route was devised [25] and later modified to obtain auxetic foam with high resilience [27] and improved stiffness [33]. A continuous process to manufacture auxetic foams by applying a biaxial rather than a triaxial pressure has also been developed [37] and it has been shown that such a process results in a highly anisotropic auxetic foam. [31]. Other investigations relating to the effect of different manufacturing parameters were also carried out, and whose results suggest that the radial and axial compression ratios are the most significant [36]. Furthermore, very recently, an alternative route to produce auxetic foams, involving the exposure of the foam to a solvent, compressing in a mould and allowing it to dry was reported [38], a process which was found to be reversible. Also recently Bianchi *et al.* [40] investigated the shape memory behaviour of auxetic foams by reconverting auxetic foams back to the conventional form and then once again to auxetic for a second time.

There have also been various attempts to model the mechanical behaviour of auxetic as well as conventional foams, leading to the development of several mechanistic models. In particular a number of 2D models were developed, including re-entrant honeycombs deforming through hinging and flexure of the ribs [55–57], conventional honeycombs deforming through stretching of the ribs [56–57], rotating rigid unit models [50, 32–33] and a missing rib model [26]. Recent work aimed at measuring the deformations of auxetic foams through 3D X-ray micro-tomography have confirmed that junctions connecting a number of ribs are observed to rotate as the bent ribs straighten under tensile loading [35] thus confirming earlier predictions [32, 33] that rotation of rigid joints and unfolding of kinks were one of the main deformation mechanisms that result in auxetic behaviour in foams. In addition to this, 3D models such as the re-entrant elongated dodecahedron model [23] and the re-entrant tetrakaidecahedron model (a cubic cell with truncated corners, more commonly known as the Kelvin cell) [24] were also analysed. In the case of conventional foams, models based on cubic cells and Kelvin cells [58–62] were also proposed. Other attempts to model conventional foam include finite element analyses of 2D [58] and 3D [61] models based on voronoi tessellations.

In this work, we study the behaviour of thermo-mechanically produced auxetic polyurethane foams at different temperatures and also their behaviour when exposed to a solvent. Knowledge of how these conditions affect the degree of auxeticity of the foam is very important as such foams are very often used under varying temperature conditions, for example in car seats where temperatures can easily exceed 75 °C in closed cars [63], or exposed to solvents for example in air filters used in fume hoods and extractors. In addition to this, we also propose a way how the foams can be subjected to high temperatures and solvent vapours while still retaining their characteristic microstructure that is required for auxeticity.

2 Experimental procedure

2.1 Preparation of auxetic foams Two samples of auxetic foams (henceforth referred to as A and B were manufactured from conventional polyurethane ether foam supplied by Crest Foams [64] with a target (nominal) ppi of 30 using the well known 'thermo-mechanical' method (see Fig. 1 for a summary of the process). The original conventional foams were each cut in a cuboid shape of dimensions 29 mm × 29 mm × 68 mm, inserted into a lubricated aluminum mould of dimensions 22 mm × 22 mm × 50 mm and heated for 10 min at 200 °C. The foams were left to cool to room temperature while still in the mould and then stretched out so as to ensure that no ribs stick to each other. The foam was then inserted back into the mould, and the heating-cooling-stretching cycle was repeated twice more, once heating again to 200 °C for 10 min and once heating to 100 °C for an hour during the last cycle. This procedure was found to produce auxetic foams in a very reproducible manner. As illustrated in Fig. 2, this process results in a

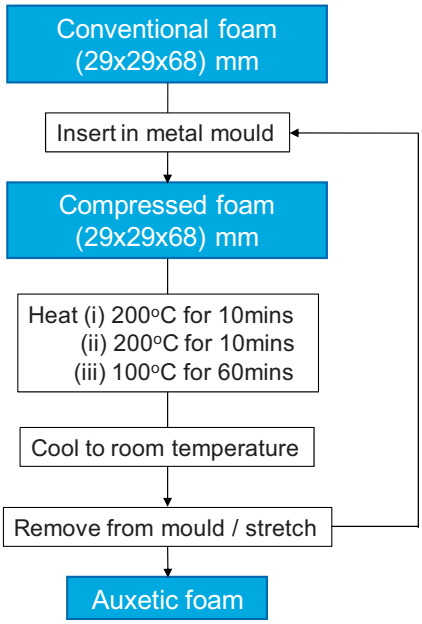

Figure 1 (online colour at: www.pss-b.com) Summary of the thermo-mechanical process used to produce the auxetic foams in this work.

significant change in the microstructure of the foams. In particular the cells which could trivially be described in terms of a conventional honeycomb conformation, changed to ones where the ribs appear as highly convoluted with numerous kinks and bends appearing along the lengths of the initially straight ribs. Such geometries are characteristic of all auxetic foams produced so far and are thought to be essential for permitting deformation mechanisms such as 'rotating rigid joints' or 'opening of re-entrant units' which result in the observed auxetic behaviour. Note that the images of the microstructures were obtained using an optical scanner operating at a resolution of 4800 dpi which was found to give satisfactory recordings of the microstructure of the foams.

Samples A and B were cut in half to produce four smaller samples (Samples A1 and A2 produced from sample A and Samples B1 and B2 produced from Sample B). These four samples were left overnight at ambient temperature

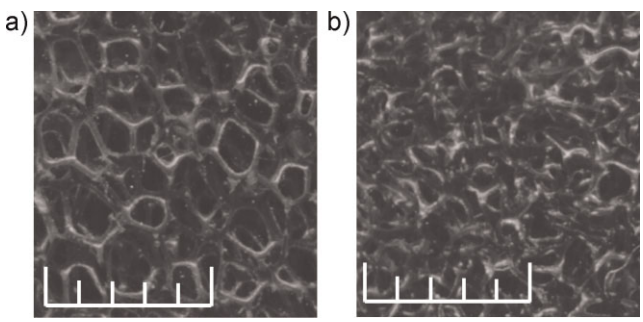

Figure 2 The microstructure of (a) the original foam and (b) the auxetic foam. In both cases, the scale indicates a distance of 5 mm.

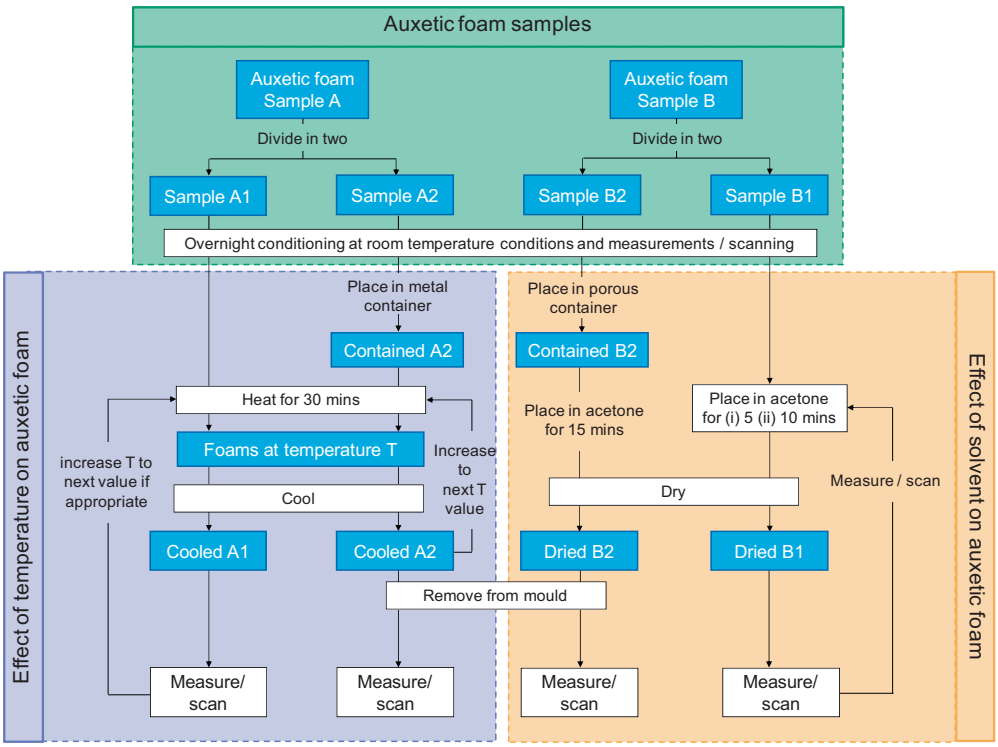

Figure 3 (online colour at: www.pss-b.com) A summary for the procedure used in testing the effect of temperature and solvent on auxetic foams.

conditions in a well-ventilated room and the dimensions were then accurately recorded.

2.2 Effect of temperature on auxetic foams Sample A2 was placed in a rigid container having dimensions which were approximately equal to that of the foam and together with sample A1 was placed in an oven at approximately 50 °C for 30 min. These two samples were then taken out of the oven, allowed to cool to room temperature and the dimensions of sample A1 were re-measured and its microstructure re-scanned. The sample was then pulled to visually assess whether it had retained its auxetic property. This process was repeated at temperatures of 90, 120, 150, 180 and 210 °C by which temperature it was observed that the size of sample A1 had reached constant dimensions approximately equal to that of the original conventional foam sample and had lost all of its auxetic character. Finally, sample A2 was taken out of the mould, re-measured and re-scanned (see Fig. 3 for a summary of the process).

2.3 Effect of solvent on auxetic foams In the meantime, sample B1 was immersed in acetone for 5 min during which process the foam was immediately (i.e. within seconds of immersion) observed to swell up. During this swelling process all the convolutions, kinks and bends that had characterized the auxetic foam were removed.

After 5 min, the foam was removed from the solvent and air dried to a constant weight. In the drying process, the foam re-shrunk slightly to a dimension which was considerably larger than that of sample B1 of the auxetic foam, but slightly smaller than its original dimensions. It was also obvious that following this simple procedure, the foam had lost all of its auxetic character. The dimensions of sample B1 were then accurately re-measured and the sample was re-scanned. This process was repeated once more with a soaking time of 10 min. Throughout these experiments, sample B2 was kept as a control in a well ventilated room at room temperature. Examination of this foam sample B2 showed that the foam dimensions remained constant and that the microstructure remained the same as that obtained immediately after the manufacture process. This sample was then placed inside a rigid porous container and immersed in acetone for 15 min, air dried to constant weight whilst still inside the container, taken out of the container and finally checked for its auxeticity, which was found to be still present and its dimensions were re-measured and its microstructure re-scanned (see Fig. 3 for a summary of the process).

3 Results and discussion Typical scans of the microstructure of the foams after being subjected to different temperature conditions are shown in Fig. 4. These results clearly show that the exposure of auxetic foam sample A1 to heat had a detrimental effect on the foam's microstructure, and hence its auxetic potential since the highly convoluted

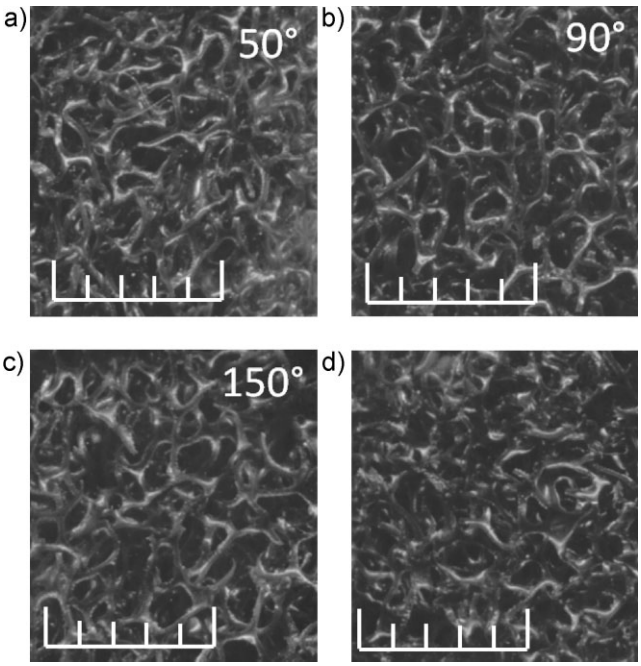

Figure 4 The microstructure of the auxetic foam when subjected to (a) 50 °C, (b) 90 °C, (c) 150 °C and (d) to the latter temperatures whilst the auxetic foam was in a rigid container of equal dimensions. The scale indicates a distance of 5 mm.

features in the microstructure were being gradually removed as the foam was re-expanding back to its original shape and the characteristic microstructure of the conventional foam as supplied by the manufacturer. In fact, the measurements made on the foam suggest that there was a gradual increase in the size of the sample and after being subjected to 210 °C, the foam was observed to have expanded by c. 87% when compared to the auxetic foam before being subjected to the high temperatures, with the result that the dimensions of this foam were more similar to that of the original conventional foam, from which the auxetic foam had been produced, than to the auxetic foam. This effect was observed to occur much more quickly when the auxetic foam was being exposed to a solvent (Fig. 5) with the swelling up process occurring almost immediately. The expansion in this case was around 85%. This loss in auxeticity could have been brought about because the interaction of the polymer with the solvent lowers the glass transition temperature of the foam so that the polymer chains are able to rearrange themselves into a conformation where the stresses in the foam microstructure are minimized [65].

These results are in accordance with recently published work by Bianchi *et al*. [40] who discussed re-conversions of auxetic foam manufactured through the heating/compression method to conventional foam which were converted again back to auxetic foams. In their work, Bianchi *et al*. report that such re-conversion to conventional foams can be performed by re-heating the unconstrained auxetic foam in an oven preheated at 200 °C and allowing it to relax to its

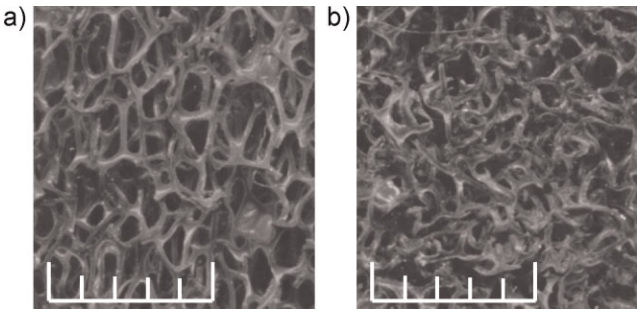

Figure 5 The microstructure of the auxetic foam when immersed in a solvent where the foam was (a) unconstrained and (b) constrained in a rigid container of equal dimensions. The scale indicates a distance of 5 mm.

original dimensions where losses in auxeticity started at a temperature of 90 °C, with the process being completed at the temperature of conversion to auxetic foam, that is, at 135 °C. Such results were also recently reported by Grima and coworkers on auxetic foam samples made from conventional polyurethane ester foam supplied by Crest Foams with a target (nominal) ppi of 35 [39].

The results of the work in this paper also clearly suggest that such detrimental effects are completely annulled if the foams are subjected to the high temperature or solvent exposure conditions in a 'contained state'. This result is clear from both the measurements of the dimensions as well as the examination of the microstructure which suggest that there is no appreciable effect on the size or microstructure with the result that auxetic characteristics of such 'contained' foams are retained.

These results are of great significance because they clearly show that the auxetic polyurethane foams manufactured using the traditional methods of manufacture have a severe limitation in the sense that they cannot be used in an uncontained state in high temperature conditions, or in applications where they are in direct contact with certain organic solvents such as acetone. Thus, for example, unless precautions are taken, auxetics foams have very limited use in automobiles that are used in hot countries where temperatures in sealed cars (e.g. cars with windows closed parked in direct sunlight) can reach very high values[1]. Similarly, such foams cannot be used in an uncontained state in situations which make them in direct contact with such solvents (e.g. in applications involving certain types of paints or in places where there are high levels of volatile organic solvents in the environment). It is also obvious that the combined exposure to high temperatures and organic solvents is likely to be even more detrimental since it is a well known fact that as a rule of thumb, the rate of chemical reactions approximately doubles per 10 °C rise in temperature.

[1] It is known that when ambient temperatures rise above 35 °C, sealed cars reach 65 °C in just 15 min.

Nevertheless, this result is also proposing a very simple method for counteracting these detrimental effects, namely that of containing the auxetic foam samples in a state of 'fixed volume'. Although *prima facie* this may look as impractical, in reality the suggested precaution could be as simple as putting the auxetic foam inside a cover which is made of a material that is unaffected by increases in temperature or solvents, such as a cover made from cotton fabrics (similar to the ones normally used in pillows or seat covers). Such contained foams can still fully benefit from the enhanced properties of auxetic materials under compression provided that the cover used is appropriate (similar to a pillow cover) since such covers will still permit the foam to change its shape without hindrance. Unfortunately, this will not be the case in tension, since the cover will impose restraints on the way the foam can deform so that it does not necessarily behave auxetically. Nevertheless, it should be emphasized that foams are not typically used in tension but only in compression: one of the main applications of auxetic foams is in seating and cushioning applications where the foam is obviously used under compression[2]. Although such 'semi-flexible' containers may not be as efficient to contain the foam in the original contained state as the ones used in this experiment, the use of such covers will permit the auxetic foam to exhibit most of its superior qualities, such as an increased resistance to indentation, whilst being protected from the detrimental effects of heat and solvent exposure with the result that its lifetime may be significantly extended. In this respect, it is important to note that in most practical applications, foams are placed inside covers for aesthetic or practical purposes, and thus, the work-around proposed here is not likely to pose any significant real limitation.

Before we conclude, it should be highlighted that not all solvents will have the same detrimental effects as shown by acetone: for example, solvents such as hexane or water do not have the same effect and more detailed and extensive studies are required so as to properly establish the effect of chemicals on auxetic foams. Also, further studies are being carried out so as to quantify the changes in the magnitude of the Poisson's ratio and modulus using tensile testing together with appropriate strain measuring techniques, which study will provide a more detailed insight on the effect on auxeticity of foams due to thermal and solvent interaction.

4 Conclusions This work has shown that the microstructure and hence the properties of auxetic polyurethane foams are significantly affected by exposure to high temperatures and exposure to chemical solvents such as acetone with the auxeticity being lost if such foam samples are exposed to these conditions in an uncontained state. A work-around to this problem is proposed, namely that of keeping the auxetic foams in a 'contained state', for example, by putting them inside a fabric cover.

Bearing in mind that as discussed in Refs. [39, 40] what is being reported here is fully reversible, i.e. the auxeticity which is lost as a result of the exposure to heat or organic solvents can be re-obtained if the foam is re-converted back to auxetic foam using any of the known standard methods [1, 25, 38], and the fact that a simple 'work around' is being proposed, i.e. that of protecting the auxetic foam with a cover that protects the foam from re-expanding, we are confident that this report will be of interest to both researchers working in the field of auxetics as well as to industrialists who may wish to make use of auxetic foams in practical applications.

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[2] For applications which require the foams to be in tension, it would be preferable for the covers to be auxetic. Otherwise, the auxetic properties may be lost. Similar observations had been made for sandwich panel composites with auxetic foam core where it is suggested that the skin of the panel must be also auxetic to fabricate it as a real auxetic composite. In such systems, if the panel employed is not auxetic, the Poisson's ratio of the composite (which would be resultant of skin and core) could be even positive and hence some of the beneficial effects that are associated with auxetic behaviour would not be observed.

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