

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
6 May 2010 (06.05.2010)

PCT

(10) International Publication Number  
**WO 2010/049511 A2**

(51) International Patent Classification:  
B29C 44/56 (2006.01)

(21) International Application Number:  
PCT/EP2009/064329

(22) International Filing Date:  
29 October 2009 (29.10.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
4236 30 October 2008 (30.10.2008) MT

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report (Rule 48.2(g))



WO 2010/049511 A2

(54) Title: A NOVEL PROCESS FOR THE MANUFACTURE OF AUXETIC FOAMS AND FOR THE CONVERSION OF AUXETIC FOAM TO CONVENTIONAL FORM

(57) Abstract: The present invention relates to a process which provides a route to convert conventional foams to auxetic foams as an alternative to existing thermomechanical processes [ WO88 /00523 ]. The present process involves taking the said conventional foam, exposing it to a correspondingly suitable solvent, removing excess solvent, compressing it, drying the foam in the compressed state only releasing it after the drying process is complete. The solvent can also be used in a process to reconvert the auxetic foam, or any other foam made auxetic by any other process to a conventional foam. This process involves exposing the foam to a suitable solvent, pulling it (sometimes not necessary), and drying the foam.

## Description

# A NOVEL PROCESS FOR THE MANUFACTURE OF AUXETIC FOAMS AND FOR THE CONVERSION OF AUXETIC FOAM TO CONVENTIONAL FORM

### Technical Field

- [1] This invention describes a new manufacturing process for making auxetic foams which may find use in a wide variety of applications including, but not limited to, ergonomic applications, protection of both inanimate objects as well as live subjects, acoustic applications, separation / filtration processes and controlled release applications.

### Background Art

- [2] Auxetic materials / structures expand laterally when stretched and conversely contract laterally when uniaxially compressed, i.e. they have a negative Poisson's ratio as opposed to most common materials, like rubber, steel, and glass, which contract laterally when compressed, leading to positive Poisson's ratios (Fig. 1). Materials may also have a Poisson's ratio of zero, in which case they neither expand nor contract when subjected to changes in external uniaxial loads.
- [3] This counter-intuitive behaviour allows for improved anchoring and self-locking properties in designing fasteners such as gaskets and rivets for tightly fitting parts and in fibres with greater fibre pull-out resistance, a property which maybe very useful in fibre-reinforced composites. This property can also be exploited in biomedical applications in sutures, prostheses and artery dilators (US5108413). They can also be used to produce composites / composite structures with an overall Poisson's ratio of zero (Japanese patent no. 6137799, 1994 ).
- [4] Auxetic materials have several other additional beneficial properties including, amongst others, an improved indentation resistance, making them suitable to use in protective equipment such as bullet proof vests, knee / elbow pads, automotive seats and packings, an enhanced ability to form doubly curved surfaces (synclastic behaviour) when subjected to bending forces, a property which is particularly desired in materials used to construct dome shaped structures, and enhanced acoustic properties, making them suitable for sound-proofing applications.
- [5] The auxetic effect in a system arises from the interplay occurring between the possible deformation mechanisms associated with the particular internal geometry of the system. This geometry may be present in the macrostructure (visible to the naked eye), microstructure (easily visible under sufficient magnification) and/or the nanostructure (the molecular geometry determined using spectroscopic or diffraction methods).
- [6] In foams, whose internal geometrical features fall within the microscale range, auxeticity arises from the microstructural arrangement of the cellular units constituting

the foam. A number of mechanisms and structures that may lead to such auxetic behaviour have been proposed. These include 'reentrant structures', 'missing rib' models and 'rotating rigid unit' mechanisms. Polymeric and metallic foams which exhibit negative Poisson's ratios have been synthesized since 1987. As disclosed in patent WO88/00523, auxetic polymeric foams were prepared from conventional open-cell foam through a thermomechanical process involving the application heat (until the temperature reaches or slightly exceeds the softening temperature) to soften the cell walls coupled with a mechanical compression of the foam in question to force the cells to alter their internal geometry in such a way that the resulting microstructure of the foam mimics one or even possibly a combination of the afore-mentioned mechanisms, so that after cooling to below the softening temperature, the cells remain 'trapped' in their new auxetic-related geometry. Such thermomechanical processes have also been developed further for scaling-up, in order to process larger blocks of foams [WO 2007052054 ] and also to provide a continuous process of preparing thermoplastic auxetic foams [WO/2007/052054].

- [7] Auxetic foams have various applications including the manufacture of ergonomic surfaces such as in cushioned chairs, mattresses and automotive seats giving them a more versatile and comfortable fit around different body parts, primarily because of their inherent improved indentation resistance and synclastic behaviour providing the ability to adapt to body curvatures, thereby surpassing conventional foams in several ways. Furthermore, deformations in auxetic foams are strain dependent and therefore allow for impacts caused by sudden blows (for example during a car crash) to be reduced in a gradual manner, potentially reducing the possibility of injuries.
- [8] The use of auxetic foams also extends to acoustic devices, for example in earphones, as disclosed in Patent US6412593, which describes the use of auxetic foams in the design of ergonomic earphones with the added benefit of improving the acoustic transmission (compared to conventional foams). Another application of auxetic foams is in separation / filtration processes as disclosed in Patent US 20060180505, which shows that by varying the load exerted upon the filter foam, the pore size can be varied according to the size of the particles that need be filtered. This offers the advantage that a single filter can be used to separate two or more components from the same mixture and additionally it also allows for improved de-fouling of the filter. Auxetic foams have also been used in garments to provide extra support and shaping (Patent US 20080032598).

### **Technical Problem**

- [9] There is a need for more energy efficient methods for converting conventional foams into auxetic foams, resulting in more economic processes.
- [10] There is a need for a manufacture process where the foam is not exposed to high temperatures.
- [11] There is a need for a process which converts auxetic foam into conventional foam.

[12] There is a need for a process which permits the manufacture of large samples of auxetic foams.

[13] There is a need for a process where the conversion occurs homogenously over the whole foam block, especially on larger foam blocks where the thermosetting process may not be equally effective throughout the block because of the foam's thermal conduction properties.

### **Technical Solution**

[14] A method of manufacturing an auxetic foam through the process of exposing the raw material (conventional foam) to a correspondingly suitable solvent which softens the foam, compressing the wet foam, and finally removing the solvent (e.g drying) from the foam whilst the foam remains in the compressed state. Once the solvent removal process is complete, the foam need not be kept in the compressed state any longer. If the solvent is recovered, this conversion process is more environmentally friendly and economic than the currently patented thermosetting processes since it does not require heating and the solvents can be reused and recycled. Furthermore, since the solvent flows in a highly homogenous manner, this process is expected to be more efficient than the currently known thermomechanical process for making large samples of auxetic foams.

[15] The solvent can also be used in a process to convert auxetic foams to conventional foams. This process involves submerging the foam in a suitable solvent, extending it (sometimes not necessary), and finally removing the solvent from the foam (e.g. air drying).

### **Advantageous Effects**

[16] The present process provides a solution to the technical problems outlined above. The use of the recoverable solvent as opposed to heat results in a more economical and environmentally friendly process for converting conventional foam into auxetic foam. This process is also much better suited for the conversion of larger foam blocks. Also, all the disadvantages associated with exposing to foams to high temperature are removed.

### **Description of Drawings**

[17] **Fig. 1:** Illustration of auxetic behaviour (negative Poisson's ratio): an auxetic expands laterally when stretched as opposed to conventional materials which have positive Poisson's ratios.

[18] **Fig. 2:** Images along (i) the cross-section and (ii) along the 'height' direction at high magnification showing (a) the conventional foam as supplied by the manufacturer of the conventional foam [DongguanDihui Foam Sponge Co. Ltd., China]; (b) the auxetic foam as manufactured by the proposed process involving solvents; (c) the auxetic foam as manufactured by the already known thermo-mechanical process, and, (d) the re-converted conventional foam produced from the auxetic foam using the proposed process. Note the similarity in the highly convoluted cell ribs in auxetic foams

obtained by the proposed and known thermo-mechanical process and the similarity between the original foam and the re-converted foam.

- [19] **Fig. 3:** A possible explanation for the observed Poisson's ratios in foams: (a) In conventional foams the positive Poisson's ratio may be explained in terms of a flexing honeycomb models. (b) In the auxetic foams, the negative Poisson's ratios may be explained (b-i) in terms of a re-entrant mechanism (flexure of ribs of re-entrant honeycombs) or (b-ii) in terms of a 'rotating rigid units' (joints) mechanism.

### **Best Mode for Invention**

- [20] This invention provides for a novel process for the conversion of conventional foams into auxetic foams by treatment with a solvent prior to subjecting to triaxial compression. To the contrary of the method disclosed in Patent WO 88/00523 credited to Roderic S. Lakes, heating of the foam to the softening temperature at any stage is not part of the methodology.
- [21] The whole process for the conversion of conventional foam to auxetic foam involves:
- [22] (1) Exposure (e.g. wetting / soaking) of the conventional foam sample in solvent ensuring that the solvent also gets in contact with the internal cells. During this step, the foam may be observed to expand in its size;
- [23] (2) Removing any excess solvent ideally leaving the foam only slightly wet;
- [24] (3) Subjecting the foam to a triaxial / biaxial compression;
- [25] (4) Drying of the foam whilst retaining the foam in the compressed state until the foam is fully dried;
- [26] (5) Where some of the above steps may be combined.
- [27] The process can be repeated for a number of times.
- [28] The advantage of the present method lies in the fact that it does not involve the use of heat implying not only a reduction in energy consumption but also that there is no need to purchase heat generating equipment and a reduced risk of foam degradation as a result of the heating process. Furthermore, large blocks of foams can be subjected to the process, in contrast to the thermomechanical process for which the size of the foam blocks that can be processed is compromised by the size and expenses of the heating equipment, i.e. the feasibility of producing large blocks of auxetic foam using the thermomechanical process depends, at least partially, on the cost of large heat generating equipment and its maintenance. This invention therefore, provides an alternative and more economical process than the thermomechanical process for the conversion of blocks of foam
- [29] For the present process, any conventional polymeric foam can be used providing that a suitable solvent, which softens / partially dissolves the polymer, is available. The transition from the conventional state to the auxetic state is due to partial dissolution / softening of the foam polymer in the solvent, i.e. the presence of the solvent is conducive to the softening / partial dissolution process which occurs concurrently with the molding effect. The chosen solvent is very much dependent on the foam material.

- Preferably, the solvent should also have a high volatility to hasten the drying process.
- [30] Compression is preferably but not necessarily applied using the mold itself, i.e. by inserting the foam inside the mold. The mold should be of the same shape as the foam being molded but with smaller dimensions so that a compression ratio of less than 1 is achieved. The extent of compression is dependent on the type of foam being used, where the smaller the pore size, the smaller the compression should be.
- [31] The mold should also be inert and permeable to the solvent to allow the solvent to evaporate easily from the foam, thereby ensuring efficient drying of the foam.
- [32] Drying of the foam (while still inside the mold) can be achieved by allowing the foams to air dry. The drying process may also be aided using other devices / methods, including but not limited to vacuum systems, forced ventilation and /or heating providing that the drying temperature remains a good way below the softening temperature of the foam being processed.
- [33] Solvents can also be used to convert (or re-convert) an auxetic polymeric foam which is obtained either through a thermomechanical process or through the process described in the present invention. In any case the conversion process for auxetic foam to conventional foam involves:
- [34] (1) Exposure of the foam to the appropriate solvent (e.g. soaking the foam in the solvent, exposure to solvent fumes);
- [35] (2) Pulling of the foam in one or more directions until the foam is in its expanded form (sometimes not necessary);
- [36] (3) Drying the foam.
- [37] This chemo-mechanical process for conversion of auxetic foams to conventional foams can be repeated for a number of times for optimum results.
- [38] For the present process of conversion from auxetic to conventional foam, any auxetic polymeric foam can be used providing that a suitable solvent, which softens / partially dissolves the polymer, is available. The transition from the auxetic state to the conventional state is due to partial dissolution / softening of the foam polymer in the solvent, i.e. the presence of the solvent is conducive to the softening / partial dissolution process which occurs concurrently with the molding effect. Clearly, this shows that the chosen solvent is very much dependent on the foam material. Preferably, the solvent should also have a high volatility to hasten the drying process.
- [39] The amount of time for which the foam is exposed to the solvent is also very critical. In particular, stiffer foams may require more time for them to become sufficiently soft for an optimum conversion to the corresponding foam. On the other hand, foams having very thin cell ribs may become significantly fragile and brittle if left for an unnecessarily prolonged time in the solvent.
- [40] Excessive stretching of foam may be counter-productive since this could lead to breaking of the cell walls which would result in a lower quality foam.
- [41] Drying of the foam can be achieved by allowing to air dry. The drying process may

also be aided using other devices / methods, including but not limited to vacuum systems, forced ventilation and /or heating.

- [42] The conversion from a conventional foam, to an auxetic foam and back to a conventional foam may be repeated for a number of times i.e. a conventional foam which is formed by the re-conversion process of an auxetic foam can be in turn reconverted to an auxetic foam.

### **Example**

- [43] In our example, auxetic foam samples were manufactured from conventional open cell 30ppi polyurethane foam (DongguanDihui Foam Sponge Co. Ltd., China), henceforth referred to as 'Foam A' using the proposed process involving solvents so as to produce 'Foam B' and also using the published thermo-mechanical process discussed elsewhere (C. W. Smith, J. N. Grima, K. E. Evans, *Acta Mater.* 2000, 48, p. 4349) to produce 'Foam C'. The auxetic foams were also re-converted back to conventional foams through the proposed method using solvents ( 'Foam B' produced 'Foam D').

- [44] In particular, samples of 'Foam B', the auxetic foam manufactured from 'Foam A' through proposed process, was produced as follows: Specimens of 'Foam A' were cut in a cylindrical form having diameter ~40mm and length ~84mm and compressed in a cylindrical form of diameter 26mm and height 55mm. These compressed foam samples were then wrapped inside a filter paper in the compressed form, placed in acetone for an hour and then air dried for eight hours whilst still in the compressed form. The result of this process was a foam (Foam B) which retained the compressed shape and also exhibited auxetic behaviour.

- [45] In an attempt to compare this form of auxetic foams to those produced through the existing manufacturing process we prepared samples of 'Foam C', an auxetic foam produced though the thermo-mechanical process as follows: Specimens of 'Foam A', which were cut in a cylindrical form having diameter ~40mm and length ~84mm, were pressed into a cylindrical mould having a diameter of 26mm and height 55mm. The foam, enclosed within the mould, was then placed in oven at 180°C for 10 minutes, removed from the mould and stretched a few times to prevent the cells from sticking together, replaced back into the mold and reheated again for a further 10 minutes, repeating the process for another time, after which the foam was heated again for one hour at 100 °C and then cooled to room temperature whilst still in the compressed form. The result of this process was a foam (Foam C) which retained the compressed shape and also exhibited auxetic behaviour, as expected.

- [46] Next we attempted to convert auxetic foams to conventional foam using solvents. For example, auxetic foams B were re-converted to the original conventional form by inserting specimens of Foam B in acetone, during which process the foams re-expand in all directions. These samples were then air dried for eight hours, a process which was found to permanently set the foams in an expanded form in a size which was comparable to that of the original foam sample. These foams, henceforth referred to as

'Foam D' were found to behave in a non-auxetic manner and to be visually very similar to the original 'Foam A'.

[47] We also examined the microstructure of the foams by viewing the foams at high magnification (e.g. the images in Fig. 2). We found that whilst the original foam (sample A, Fig. 2a) is characterised by unit cells which may be described in terms of the traditional conventional foam models, i.e. 3D Kelvin cells or in terms of much simpler 2D conventional honeycomb model, the auxetic foams (samples B and C Fig. 2 b and c respectively) are characterised by a more complex geometry where the straight ribs found in the original conventional foam now appear highly bent as a result of extensive buckling which occurs during the compression process that is characteristic of both the traditional and the novel manufacturing process. In fact, irrespective of the manufacturing process, the images of the cells in the auxetic foam were found to contain the essential features to permit them to deform through the 're-entrant mechanism' [e.g. L. J. Gibson and M. F. Ashby, *Cellular Solids: Structure and Properties*, 2nd edn. Cambridge University Press, 1997; I. G. Masters and K. E. Evans, *Composite Structures* 1996, 35, 403] or the 'rotation of rigid joints' [J. N. Grima, R. Gatt, N. Ravirala, A. Alderson and K. E. Evans, *Mater. Sci& Eng. A* 2006, 423, p. 214; J. N. Grima, A. Alderson and K. E. Evans, *J. Phys. Soc. Jpn.* 2005, 74, p. 1341] mechanisms which, as discussed elsewhere, can explain the observed auxetic behaviour (see Fig. 3). In this respect it is important to note the similarities between the images related to Foam B and Foam C which suggest that the two processes result in very similar products. Furthermore, in an attempt to verify the observed auxeticity we took measurements of the Poisson's ratios from measurements of the diameter and lengths of the foams at various applied strains. These measurements clearly confirm that whilst the original foam as supplied by the manufacturer (sample A) exhibits a positive Poisson's ratio, foams B and C exhibit negative Poisson's ratios (auxetic) of a similar magnitude. The similarity in these Poisson's ratio measurements together with the similarity in the microstructure observed in Foams B and C confirm that the novel chemo-mechanical process is as effective as the conventional thermo-mechanical process for production of auxetic foam as both processes produce similar products. This is very significant as it suggests that all the beneficial effects that have been associated with the auxetic foams manufactured through the conventional thermo-mechanical method will also be exhibited by our auxetic foams produced by the novel chemo-mechanical process.

[48] The measurements of the Poisson's ratio made on samples of conventional foams made from previously auxetic foam through the solvent mediated method (e.g. 'Foam D') confirmed that such foams have positive Poisson's ratios of comparable magnitude as those of the original foam. Also, when we examined the images of the re-converted foam (e.g. those of sample D, see Fig. 2d) we found that the ribs are once again straight and the cells in these foam samples are in a form which may be well described by the

traditional conventional foam models thus explaining the observed change in the sign of the Poisson's ratio from negative to positive. We also observed big similarities between the microstructures of the original conventional foams (Foam A) and the conventional foams made from previously auxetic foam through the proposed method ('Foam D') which suggest that the re-conversion process, when applied to auxetic foams is very effective.

[49] It is of course understood that the present invention is described by way of example only and it is not intended to be restricted to the examples described here. In particular, these processes may be performed using different types of foams and different types of appropriate solvents or mixtures of solvents provided that the solvent/s used will result in softening / partial, but not full, dissolution of the foam. Also, it is possible to combine all / parts of the 'solvent processes' and the 'thermal process'.

[50] Also, it is possible to perform multiple conversions, i.e. 'conventional to auxetic to conventional'; 'auxetic to conventional to auxetic'; 'conventional to auxetic to conventional to auxetic'; 'auxetic to conventional to auxetic to conventional'; 'conventional to auxetic to conventional to auxetic to conventional' and so on.

#### **Industrial Applicability**

[51] The invention has applicability to the protection industry as well as the seating industry, acoustic applications, in separation / filtration applications and controlled release applications

## Claims

- [1] A reversible process for the preparation of auxetic foams (foams that exhibit a negative Poisson's ratio) from conventional foams where the process for the preparation of auxetic foams involves: a. Exposure (e.g. wetting / soaking) of a conventional foam (i.e. foam that has a positive Poisson's ratio) thoroughly in a suitable solvent; b. removing any excess solvent ideally leaving said foam only slightly wet; c. applying a triaxial / biaxial compression to the foam; d. drying the foam in its compressed state; e. removing the said compression; f. repeating the process one or more times (sometimes not necessary) whilst the process for the preparation of conventional foam from auxetic foam involves: a. Exposure of the auxetic foam to an appropriate solvent for a suitable amount of time; b. Pulling of the foam in one or more directions until the foam is in its expanded form (sometimes not necessary); c. Drying the foam using an appropriate method; d. Repeating the process one or more times (sometimes not necessary).
- [2] A process as claimed in claim (1) where the mold for making the auxetic foam has the same corresponding shape as the foam, including cylindrical and cuboidal shape, but with smaller dimensions such that the compression ratio is less than 1 where the mold is permeable to the solvent.
- [3] A process for converting a conventional foam to an auxetic foam as in claims (1) and (2) where the foam is inserted in an appropriate mold, after which it is exposed to the appropriate solvent (e.g. soaked) and dried completely.
- [4] A process as claimed in any preceding claim with a solvent exposure time (e.g. soaking time) that varies between a few seconds and several minutes to longer times including hours.
- [5] A process as claimed in any preceding claim where the foam is left to air dry or where drying is aided by other techniques including: applying a vacuum, passing a flow of air / inert gas or heated air / inert gas through the mold and foam, or by heating the foam within the mold ensuring that the temperature remains below the softening temperature.
- [6] A process as claimed in any preceding claim where the process or parts of it are combined or replaced with the existing thermo-mechanical process or parts of it.
- [7] A process as claimed in claims (1) to (6) where the solvent has the property of softening the foam including acetone, chloroform, toluene, ethylacetate and blends thereof.
- [8] An auxetic foam made according to the process in any preceding claim using any one of methods claimed in claims (1) to (7).
- [9] An auxetic foam made using any one of the processes described in claims (1) to (7) wherein the foam is chosen from the group comprising polyurethane; polyesters including polybutylene terephthalate and polyethylene terephthalate; polymers of ethylene, propylene, butene-1, isobutene, vinyl chloride, vinylidene

chloride, ethylacrylate, methyl methacrylate, styrene, .alpha.-methyl-styrene, (t-butyl) styrene, ethyl cellulose, methyl cellulose, ethylene/vinyl acetate copolymer, ethylene/acrylic acid copolymer, ethylene/methyl methacrylate acid copolymer, ionomer salt of such acid copolymers; and blends thereof.

[10] A filter, cushioning material or clamping material comprising an auxetic foam according to any one of claims 8 or 9.

[Fig. 1]

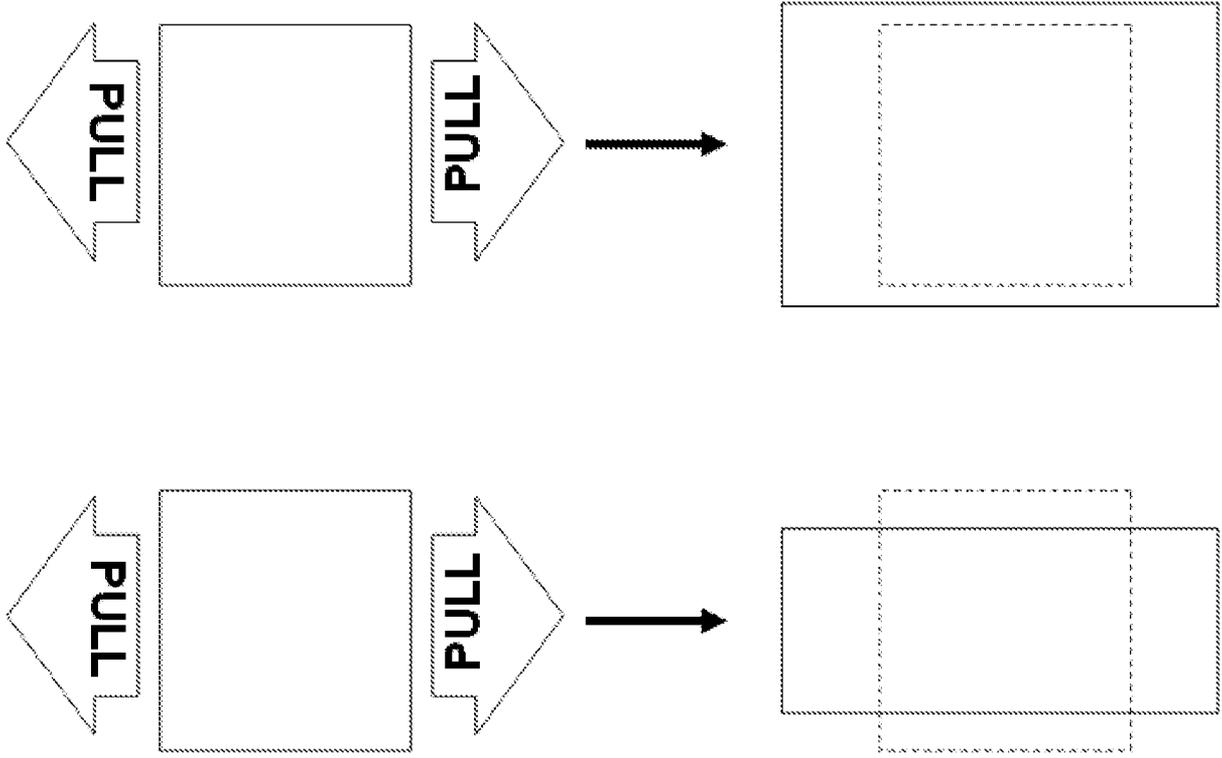
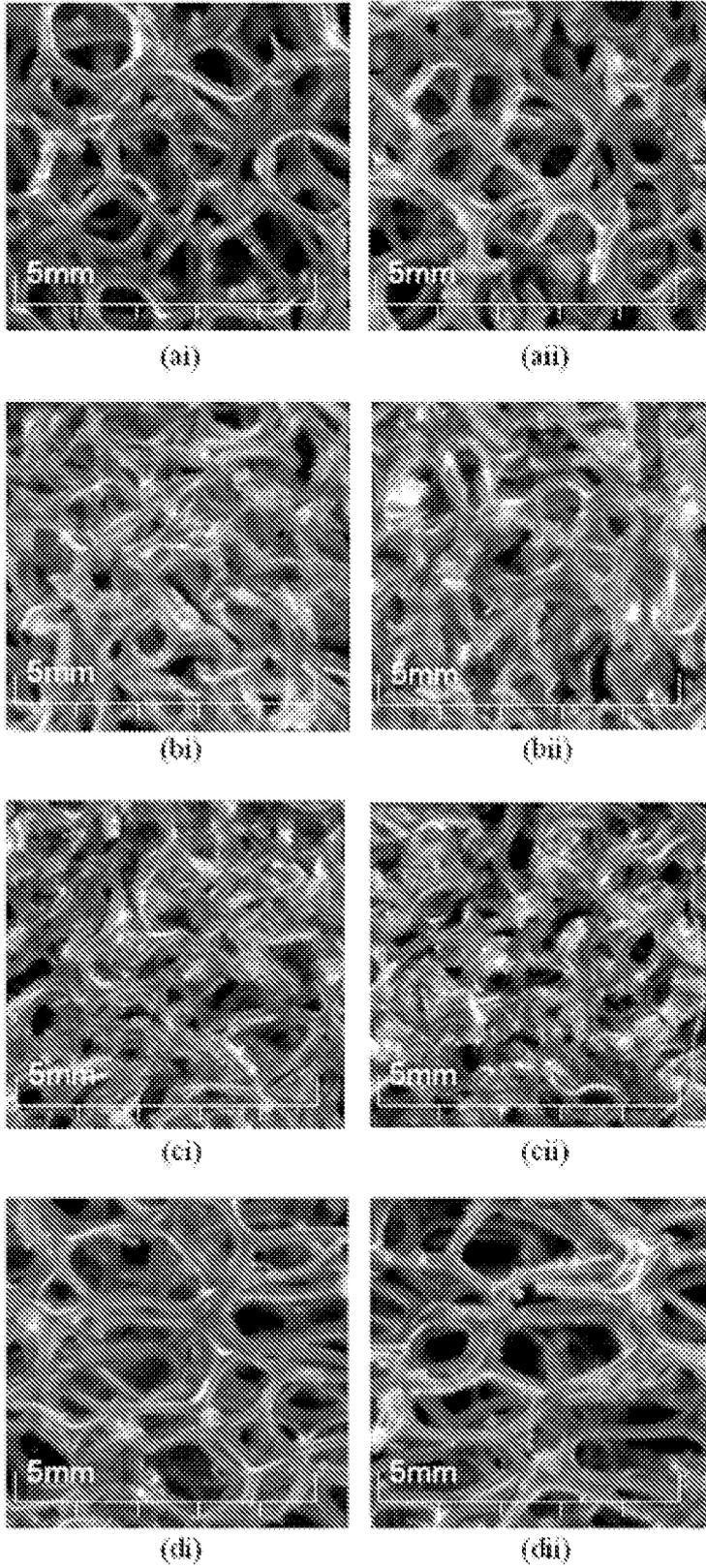


Fig. 1

[Fig. 2]



**Fig. 2**

[Fig. 3]

(a) CONVENTIONAL FOAM

(b) AUXETIC FOAM

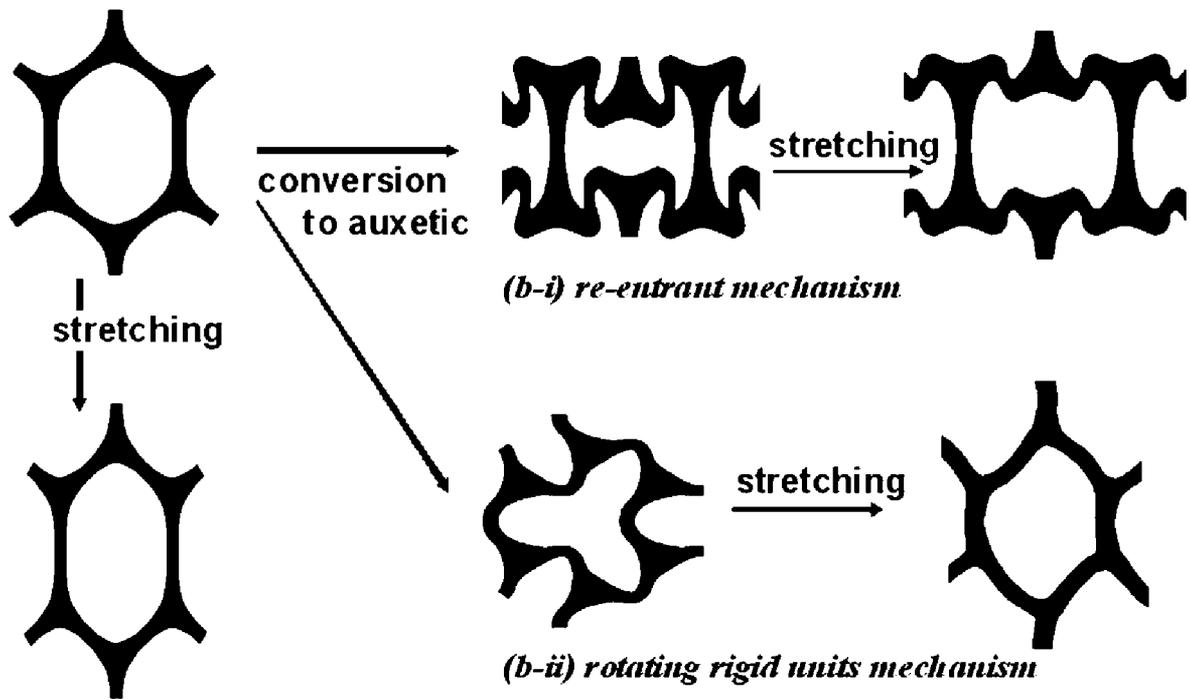


Fig. 3