Auxetic Structures for Variable Permeability Systems

J. Rasburn, P. G. Mullarkey, and K. E. Evans
School of Engineering and Computer Science, University of Exeter, Exeter, EX4 4QF, U.K.

A. Alderson
Bolton Institute, Faculty of Technology, Bolton BL3 5AB, U.K.

S. Ameer-Beg and W. Perrie
BNFL Research and Technology, Preston PR4 0XJ, U.K.

Strength and stiffness are two important mechanical properties with which many people are familiar, but equally important is the Poisson's ratio, the ratio of the change of width of a material to a change in its length. Control of this less familiar property by appropriate design of materials is likely to benefit a host of exciting physical, chemical, and engineering applications. In particular, a porous material with a *negative* Poisson's ratio proffers possible solutions to problems encountered in the fields of filtration and permeability by providing a means of altering pore size, either by an applied load or automatically, owing to pressure variations.

Poisson's ratio describes the way in which a material deforms laterally when subjected to a longitudinal deformation. It is defined as the negative ratio of transverse strain to longitudinal strain. In everyday experience, one is familiar with materials with positive Poisson's ratio, that is, on being stretched, they become thinner. An elastic band provides a good illustration of this effect. Over the last decade, materials with negative Poisson's ratio have engendered increasing interest (Lakes, 1987, 1993; Evans, 1990, 1991; Alderson, 1999). Such materials widen when stretched or, conversely, narrow when compressed, and have been termed *auxetic* (Evans et al., 1991).

This type of behavior appears strange and counterintuitive at first sight. However, if considered in the context of all materials with Poisson's ratios less than 0.5, auxetic materials can then be seen as extreme cases of materials that undergo an increase in volume upon stretching. This classification would encompass most metals, polymer foams, and complex composites such as wood and fiber-reinforced plastics.

An increase in volume upon stretching raises the issue of the homogeneity of the material. A volume increase can be effected if the material comprises distinct elements or substructures that do not pack together as well in the stretched state as they do in the undeformed state. In the case of a polymer foam, the structural elements are fairly obvious in the ribs or walls of the foam cells. These also define the voids in the material. In the fiber-reinforced composite, the important elements are the stiff fibers and, instead of voids, the plastic matrix serves as the low-stiffness counterpart to the fibers. At the atomic level, atoms or molecular structures can be viewed as the structural elements. Indeed, anisotropic, negative Poisson's ratios have also been observed (Yeganeh-Haeri et al., 1992) in the α-cristobalite polymorph of crystalline silica.

Recently we have been exploring this area using specially fabricated honeycomb structures. These have been fabricated by a carefully controlled visible and near-UV femtosecond pulsed laser ablation (Kumagai et al., 1994; Kruger and Kautek, 1996) process on polymer sheets. The polymer was a flexible (at room temperature) acetate polymer (Hewlett-Packard Part Number: HP C2936A). The structures are shown in Figure 1, which also provides a convenient illustration of an auxetic mechanism. The indicated *x-y* axes are an arbitrary reference system that aids in quantitative analysis of the honeycombs' properties using expressions published previously (Gibson et al., 1982) and from this laboratory (Masters and Evans, 1996). To appreciate the auxetic mechanism, consider the consequence of a tensile force directed along the *y*-direction in Figure 1b. By a hinging motion, the diagonal struts will rotate toward the horizontal. The system as a whole expands laterally, and hence exhibits a negative Poisson's ratio. This would also happen if a tensile force were applied along the *x*-direction, although it should be emphasized that the actual value of the Poisson's ratio is markedly anisotropic for these honeycombs. On the other hand, *x*- and *y*-directed tensile forces applied to the honeycomb structure of Figure 1a would generate negative strains in the relevant transverse direction, and hence this system has a positive Poisson's ratio. We describe the honeycomb of Figure 1a as having *conventional* hexagonal cells, while Figure 1b has *reentrant* cells.

Mechanical characterization of these structures has employed a universal testing machine equipped with a digital

Correspondence concerning this article should be addressed to K. E. Evans.

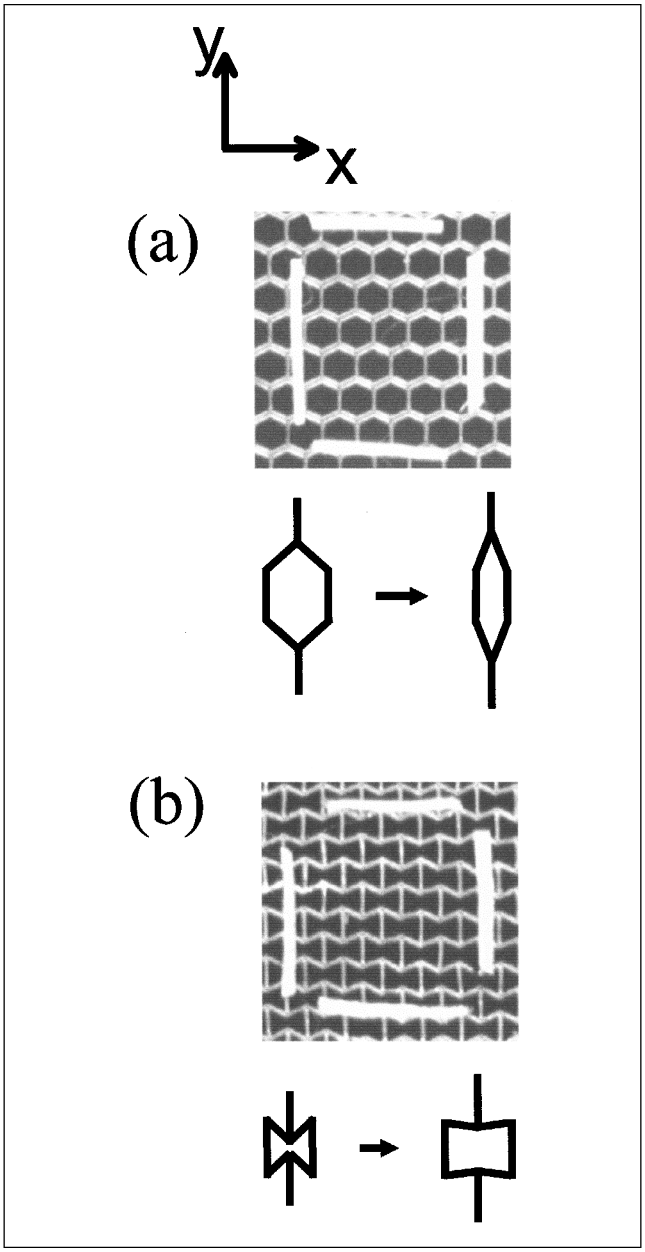

Figure 1. (a) Conventional hexagonal honeycomb as viewed through a digital videoextensometer system; (b) the reentrant honeycomb structure viewed under similar testing conditions as the specimen in (a) with associated deformation below.

In (a) the prominent white strips are fiducial markers, used for measuring average strains, and are of approximate length 4 mm; "hinging" deformation in response to a vertically applied strain is shown below the photograph.

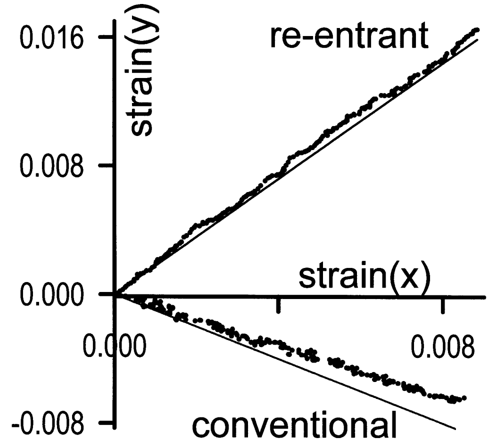

Figure 2. Transverse strains of the reentrant and conventional honeycombs resulting from applied longitudinal strain in the *x*-direction.

The solid lines are predicted on the basis of a combination of flexure, hinging, and stretching mechanisms of the constituent ribs.

video recording facility. This enables visual tracking of the movement of designated targets, such as the fiducial markers evident in Figure 1. Digital output of force and target position are delivered, and hence moduli and x- and y-strain values are determined. Typical data are shown in Figure 2 and summarized in Table 1. Here, reentrant and conventional honeycombs have each been stretched in the x-direction. The consequent strain in the y-direction has been plotted on the ordinate. It is very clear that the reentrant structure widens upon being stretched, and is therefore auxetic. The area described by each of the "bow-tie" or "butterfly" structures increases during stretching. The conventional structure narrows upon being stretched, that is, it has a positive Poisson's ratio.

The Poisson's ratio, υ, at a given applied strain in each case is determined from the slope of the strain–strain curve at that strain (Alderson et al., 1997). For the honeycombs studied here, essentially strain-independent υ's are observed.

The lines in Figure 2 are values of strain predicted on the basis of expressions derived from consideration of the underlying processes in the response of the honeycombs to small applied strain. This response comprises a combination of flexure (Gibson et al., 1982), hinging, and stretching of the ribs (the concurrent mechanism) (Masters and Evans, 1996). The membrane geometries (determined by optical microscopy) and the mechanical properties of the polymer material forming the ribs (obtained by tensile testing of a sample of the unablated polymer) were used in the model expression. In general, agreement is good. Departures from linear elasticity, anisotropy of the starting polymer film modulus, and slippage of the fiducial markings are possible sources of uncertainty. Measured values of h/l (the ratio of the length of the vertical ribs to that of the diagonal ribs in Figure 1), θ (the honeycomb angle), the Young's Modulus ($E_{y/x}$), and Poisson's ratio ($\upsilon_{xy/yx}$) relevant to each direction are given in Table 1. With the exception of E_x and υ_{yx} for the auxetic honeycomb, the observed Poisson's ratios and Young's moduli agree within the calculated uncertainties with the predicted values. Values for the force constants associated with flexure (K_f), hinging (K_h), and stretching (K_s) of the ribs in the model for the deformation involving concurrent deformation mechanisms were derived from the honeycomb rib dimensions and the intrinsic properties of the polymer material. Assuming a combination of rib hinging and rib flexure,

Table 1. Experimental and Calculated Stiffnesses and Poisson's Ratios for Two Honeycombs of Figure 1

Honeycomb	h/l	$\theta/°$	E_x/GPa	E_y/GPa	υ_{xy}	υ_{yx}	K_f/K_h	K_f/K_s
Conventional								
Experimental	1.2	+23	0.23	0.130	0.86	0.6		
	±0.2	±2	±0.04	±0.001	±0.06	±0.1		
Predicted			0.15	0.09	1.0	0.6	0.18	0.06
			±0.08	±0.05	±0.2	±0.1	±0.08	±0.02
Auxetic								
Experimental	1.45	−23	0.127	0.032	−1.82	−0.51		
	±0.05	±2	±0.006	±0.006	±0.05	±0.01		
Predicted			0.08	0.021	−1.8	−0.44	±0.08	0.026
			±0.02	±0.005	±0.1	±0.04	±0.01	±0.003

flexure is the more compliant mechanism, that is, K_f/K_h is small. Hence, flexure is the predominant process of deformation. Similarly, flexure predominates when a combination of stretching and flexure is assumed.

After thorough characterization of the mechanical properties of the honeycombs, we then turned to experiments on a simple model system in order to explore the possibility of exploiting the increase in pore area that occurs on stretching the auxetic honeycomb. The motive for this stems from situations where a filter system has become blocked by ingress of particulates into the body of the filter, thus clogging the pores. Deformation of the system in order to increase its permeability and thus promote clearance of the blocking particulates from its pores may offer an improved alternative to other methods of cleaning or defouling filters. This could lead to cost savings and environmental benefits as a result of improved filtration efficiency, fewer filters required, a reduction in waste or spent filters, and less plant downtime owing to filter replacement operations. This would be particularly beneficial where filters are required to operate in harsh environments, such as, for example, highly radioactive cells. Alternatively, a different grade of filter may be required for a given installation at a given moment in a process; the ability to alter the filter's characteristics by suitable mechanical intervention, yet without a wholesale replacement of the active element, would be a useful facility.

We found that glass chromatography beads (40 mesh) with a diameter of 0.42 mm fitted snugly into the pores of the reentrant auxetic honeycomb, two beads per bow tie. This system was examined using video footage of a sample mounted in a horizontal tensile straining stage. This allowed us to stretch the honeycomb when it was laid flat and covered in a single layer of glass beads, as shown in Figure 3a. As expected, on stretching the auxetic honeycomb, the beads began to fall through (Figure 3b) and, by virtue of the close matching of pore size and bead diameter, this occurred for small deformation similar to those used in the mechanical characterization tests. A large and damaging plastic deformation, in which the characteristics of the honeycomb would probably depart from those previously evaluated, was therefore avoided.

Significantly, the rate of clearance with applied strain of the honeycomb's pores was observed to be dependent on the stretching direction, and by implication, therefore, the value of the Poisson's ratio. Specifically, stretching in the x-direction (characterized as having Poisson's ratio ~ -1.8) produced a markedly more rapid clearance with increasing strain than stretching in the y-direction (Poisson's ratio originally ~ -0.5). This is shown in Figure 4, where the number of pores remaining blocked is plotted as a function of applied strain. It should be noted that each data set is the product of numerous repeated tests. The data set showing the steeper rate of descent corresponds to applied strains in the x-direction ($\upsilon \approx -1.8$); the other set corresponds to applied y-strains ($\upsilon \approx -0.5$). This is particularly encouraging, since it suggests that the clearing effect is indeed attributable to the rate of pore opening and not simply the result of any minor agitation that may accompany the test.

Interestingly, the honeycombs considered in this article are analogous to some of the models for "springy" polymers (Noether and Whitney, 1973, and the "paper bell" model of Clark, 1973), in which the vertical ribs in the honeycomb cor-

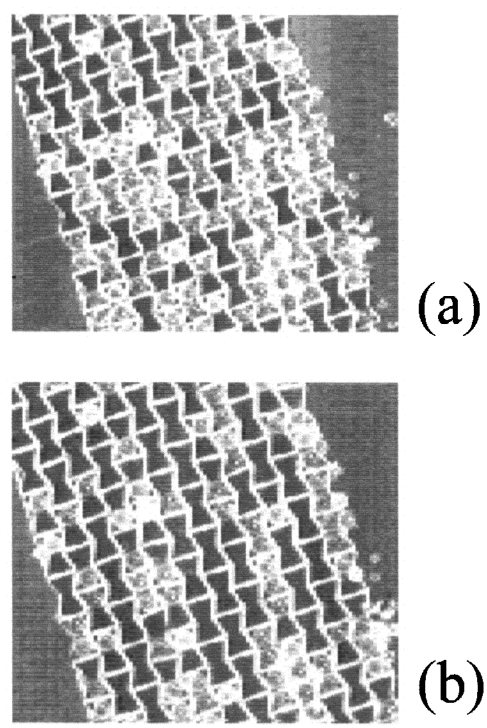

Figure 3. (a) Auxetic honeycomb loaded with glass beads; (b) after applying strain of about 1% in the x-direction to loaded honeycomb in (a).

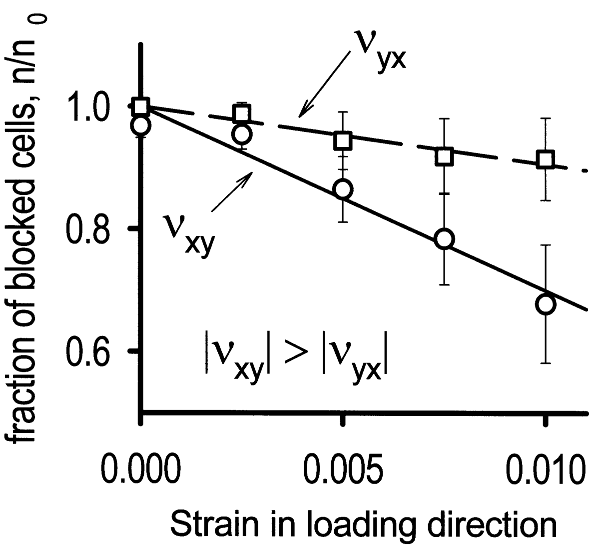

Figure 4. Ratio of number of blocked cells (n) to initial number of blocked cells (n_o) vs. applied strain.

The labels indicate which Poisson's ratio is operative during the test.

respond to interlamellar tie molecules in springy polymers. Springy polymers are used in membranes where control of pore size is important. A *three-dimensional* demonstration of the connection between Poisson's ratio and permeability is implicit in the studies on springy polymers reviewed by Cannon et al. (1976). There, polymer fibers that maintain nearly constant fiber diameter during tensile deformation (that is, having Poisson's ratios of ca. zero) were characterized by porosimetry and gas absorption methods at a range of fixed extensions (Quynn and Brody, 1971). Pronounced increases in porosity and available surface area and specific volume with extension were evident for these fibers compared to a typical elastomer. The permeability of springy polymer films has been found to increase markedly with extension (Clark, 1973). We are not aware of the existence of auxetic springy polymer fibers or films.

The principle behind these experiments may then have far-reaching implications for filter materials other than simple honeycomb membranes and also many other scenarios involving some sort of inclusion, not just filtration. For example, being able to manipulate by mechanical means the accessibility of pore space in stable, auxetic coordination solids having molecular-sized cavities and pathways could be relevant in sensor and molecular-sieve applications. It may also be of benefit to situations where the phase of the guest material is affected by the volume of the confining space, an example being the crystallization temperature of a solvent inside a porous medium (Jackson and McKenna, 1990; Klein and Kumacheva, 1995). The possibilities for auxetic structures in physicochemical applications thus extends to both the macroscopic and microscopic levels.

Acknowledgment

The authors are grateful to BNFL for funding this research.

Literature Cited

Alderson, A., "A Triumph of Lateral Thought," *Chem. Ind.*, (10), 384 (1999).

Alderson, K. L., A. Alderson, and K. E. Evans, "The Interpretation of the Strain-Dependent Poisson's Ratio in Auxetic Polyethylene," *J. Strain Anal.*, **32**, 201 (1997).

Cannon, S. L., G. B. McKenna, and W. O. Statton, "Hard-Elastic Fibres: A Review of a Novel State for Crystalline Polymers," *J. Poly. Sci., Part D, Macromol. Rev.*, **11**, 209 (1976).

Clark, E. S., "A Mechanism of Energy-Driven Elasticity in Crystalline Polymers," *Structure and Properties of Polymer Films*, R. W. Lenz and R. S. Stein, eds., Plenum Press, New York (1973).

Evans, K. E., "Tailoring the Negative Poisson's Ratio," *Chem. Ind.*, **20**, 654 (1990).

Evans, K. E., "Auxetic Polymers: A New Range of Materials," *Endeavour (New Ser.)*, **15**, 170 (1991).

Evans, K. E., M. A. Nkansah, I. J. Hutchinson, and S. C. Rogers, "Molecular Network Design," *Nature*, **353**, 124 (1991).

Gibson, L. J., M. F. Ashby, G. S. Schajer, and C. I. Robertson, "The Mechanics of Two-Dimensional Cellular Materials," *Proc. Roy. Soc.*, **A382**, 25 (1982).

Jackson, C. L., and G. B. McKenna, "The Melting Behaviour of Organics Materials Confined in Porous Solids," *J. Chem. Phys.*, **93**, 9002 (1990).

Klein, J., and E. V. Kumacheva, "Confinement-Induced Phase-Transitions in Simple Liquids," *Science*, **269** (5225), 816 (1995).

Kruger, J., and W. Kautek, "Femtosecond-Pulse Visible Laser Processing of Transparent Materials," *Appl. Surf. Sci.*, **96-98**, 430 (1996).

Kumagai, H., K. Midorikawa, K. Toyoda, S. Nakamura, T. Okamoto, and M. Obara, "Ablation of Polymer-Films by a Femtosecond High-Peak-Power Ti Sapphire Laser at 798 nm," *Appl. Phys. Lett.*, **65**, 1850 (1994).

Lakes, R. S., "Foam Structures with a Negative Poisson's Ratio," *Science*, **235**, 1038 (1987).

Lakes, R. S., "Advances in Negative Poisson's Ratio Materials," *Adv. Mater.*, **5**, 293 (1993).

Masters, I. G., and K. E. Evans, "Models for the Elastic Deformation of Honeycombs," *Compos. Struct.*, **35**, 403 (1996).

Noether, H. D., and W. Whitney, "X-Ray Diffraction and Morphology of Crystalline, Hard, Elastic Materials," *Kolloid-Z.U.Z. Polym.*, **251**, 991 (1973).

Quynn, R. G., and H. Brody, "Elastic 'Hard' Fibres," *J. Macromol. Sci.-Phys.*, **B5**, 721 (1971).

Yeganeh-Haeri, A., D. J. Weidner, and J. B. Parise, "Elasticity of Alpha-Cristobalite—A Silicon Dioxide with a Negative Poisson's Ratio," *Science*, **257**, 650 (1992)

Manuscript received Mar. 27, 2000, and revision received Feb. 28, 2001.