Brief Research Report

MOLECULAR MODELLING OF AUXETIC ZEOLITES*

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Materials with a negative Poisson's ratio, i.e. auxetic materials, exhibit the unexpected property of becoming wider when stretched and thinner when compressed (Fig. 1) [1]. This rare property, which is very much dependent on the geometry of the material, results in the enhancement of various macroscopic properties of the material and makes auxetics superior to their conventional counterparts in many practical applications [2].

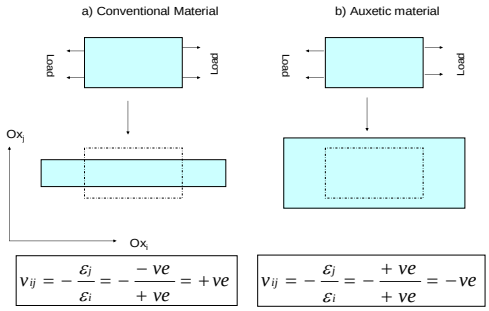

Figure 1: Comparison of the effect of stretching on a) a conventional material, and b) an auxetic material. The dotted lines represented the original shapes.

It was recently shown through preliminary modelling studies [3] that some zeolite frameworks may exhibit this unusual property. The preliminary research on zeolites had defined that those zeolites that exhibit auxetic properties deform *via* particular mechanisms in response to applied stress. These include the rotating squares mechanism and the rotating triangles mechanism, where the corners of the squares or triangles are oxygen atoms [4].

Unfortunately, these preliminary studies relied on various assumptions, e.g. no cations or interstitial water molecules were included, assuming therefore that such species would have little or no effect on the deformation mechanism.

This paper re-examines this problem and a methodology for simulating zeolites with cations and water molecules is described. This methodology was applied on a number of zeolites with the scope of assessing the contribution of cations and water molecules on the mechanical properties and on the way the system responds to applied loads (i.e. the deformation mechanism). The study was conducted using molecular modelling i.e. techniques of visualisation and computational methods in order to study or predict the properties of molecules. The zeolite structures were simulated through force-field based simulations using the commercially available molecular modelling software Cerius^2 [5]. In particular, two zeolites were studied, NAT and EDI which in the preliminary study were found to exhibit auxetic behaviour through a rotating squares mechanism (Figure 2).

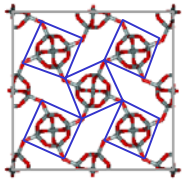

Figure 2: The rotating squares mechanism observed in the zeolite: NAT in the (001) plane.

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It was found that cations and water molecules do play an important role on the Poisson's ratios although in most cases, the auxetic behaviour is retained. While cations reduced the auxeticity of the structure by a small degree, the addition of water molecules had a greater effect rendering the structures less auxetic to the extent that auxeticity is only observed off-axis (see Fig. 3).

This observation may be explained by the fact that the structures were also observed to be stiffer with the inclusion of water and cations. Essentially, the water and cations seemed to be 'in the way', preventing the 'hinging oxygen atoms' from deforming as much as was possible in response to loading.

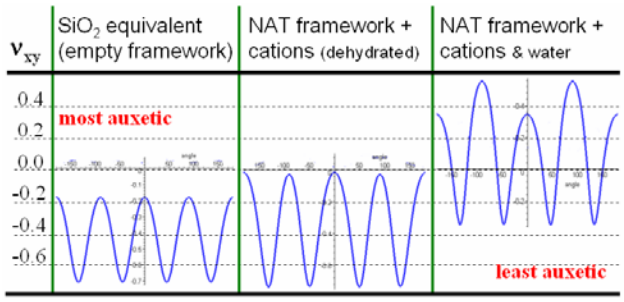

Fig. 3: The 'reduced' auxeticity in NAT as the amount of interstitial species is increased. Note that whilst the SiO_2 equilvealent of NAT without any interstitial species is auxetic for loading in any direction in the (001)-plane (the xy-plane), the real zeoilite (i.e. NAT framework + cations and water) is only predicted to be auxetic at 45^o off-axis.

The discovery that some zeolites exhibit a negative Poisson's ratio is likely to have various important commercial repercussions, and, in particular, the possibility of having molecular sieves where the pore size can be controlled is more likely to become a reality [6].

References:

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[4] J. N. Grima and K. E. Evans *J. Mat. Sci. Lett.*, **19** (2000) 1563-1565.

[5] Molecular Simulations Inc. (MSI), San Diego, California, currently incorporated within Accelrys (http://www.accelrys.com).

[6] A. Alderson, J. Rasburn, K.E. Evans, J.N. Grima, *Membrane Technology*, **137** (2001) p. 6-8.