

Modeling Entrapment and Release Structures - an Auxetic Polymeric Honeycomb Host-Guest System

Negative Poisson's ratio molecular networks may find application where the entrapment and release of active molecular species are required. Examples include the controlled release of drugs in the biomedical industry, selective entrapment in molecular sieves, catalysis and ion-exchange processes in the chemical engineering and nuclear industries, and the control of potentially toxic nanoparticles.

Researchers at the Universities of Bolton and Exeter in Great Britain and the University of Malta have used of Accelrys' Sorption module to model the mechanical properties and transport properties of polymeric honeycombs containing C_{60} and C_{70} guest molecules¹. Modeling was invaluable as these structures are difficult to synthesize.

"The molecular modeling software enabled us to predict the structure, mechanical and mass transport properties of idealized polymeric networks that currently are proving challenging from a synthesis viewpoint - so the work could not currently have been performed in an experimental context," said Professor Anderson, Centre for Materials Research & Innovation, The University of Bolton.

"In addition to the issues of synthesis, there are practical issues relating to making samples of sufficient size for mechanical testing and then the design of appropriate experiments for the mass transport work - all of which are possible in principle but will be significant tasks in reality," he continued.

The mechanical properties of the honeycombs were predicted to include negative on-axis Poisson's ratios. Simulations of the loading of C_{60} and C_{70} guest molecules into the host framework demonstrated the potential for tunable size selectivity within the host framework.

Polymeric honeycombs have been used to demonstrate enhanced cleanable or tunable filter performance² due to the fact that they have a negative Poisson's ratio, the so-called auxetic effect. Auxetic materials are an unusual class of materials with a number of commercially significant applications. The enhanced abilities arise due to the increased pore size and/or shape change that occurs when an auxetic material is placed under uniaxial load: under stress the pore size will actually increase. Such materials can switch between entrapment and release of sorbates as a function of external pressure alone. At the molecular level, this provides interesting possibilities for the controlled release of active agents such as drug molecules and enzymes.

The molecular honeycombs considered in this work have pore dimensions on the order of the diameters of "buckyballs" and also provide idealized systems with which to address current concerns over the mass transport of potentially toxic fullerene and other nanoparticles³.

Module used

Materials Studio Sorption

Industry sectors

Catalysis
Pharmaceutical
Nuclear
Separations

Organizations

University of Bolton
University of Exeter
University of Malta

Results

C2-OFF and the Dreiding force field⁴ were used to predict the mechanical properties of conventional and so-called re-entrant hexagonal molecular polymeric honeycomb networks, which are shown in Fig 1. Previous work suggests that these structures would exhibit a negative Poisson's ratio.

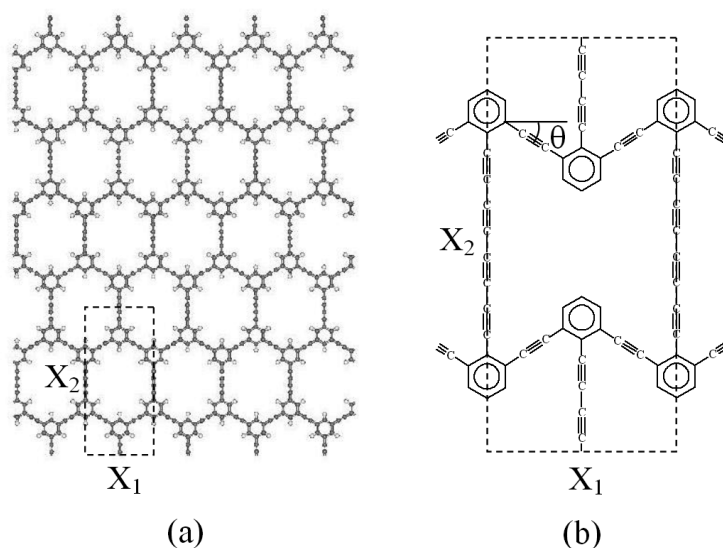


Figure 1. (a) conventional honeycomb network: '1,2-flexyne'; (b) re-entrant honeycomb network: '1,4-flexyne'

Figure 1(a) shows a conventional honeycomb while in figure 1(b) a sub-unit of the re-entrant honeycomb is displayed. Note that in the re-entrant case, three acetylene groups are connected to adjacent benzene ring carbons, while in the conventional structure the acetylenes are connected to alternate benzene ring carbon atoms. The nomenclature for the honeycomb networks is (n,m)-flexyne and (n,m)-reflexyne, respectively, where n and m are the respective number of acetylene links in the diagonal and vertical branches. The conventional molecular honeycomb is then called (1,2)-flexyne, and the re-entrant molecular honeycomb (1,4)-reflexyne.

The force field calculations confirm that (1,4)-reflexyne possesses negative Poisson's ratio, whereas (1,2)-flexyne has positive Poisson's ratio. A specific re-entrant honeycomb ((2,8)-reflexyne) was selected for detailed study. This material is not simply auxetic; its properties are stress-dependent and actually switch from negative to positive Poisson's ratios at a critical loading stress along the X_2 direction.

Sorption calculations of the loading of C_{60} molecules and the simultaneous loading of C_{60} and C_{70} molecules into a (2,8)-reflexyne indicate that the loading is stress-dependent (Fig.2a). The entrapment and release of guest molecules within the (2,8)-reflexyne is determined by variations in the pore size and shape. Under increasing stress, pore size increases accommodating a greater load. At a critical stress, however, the Poisson's ratio becomes positive, pore size decreases, and the load drops dramatically. Similar studies with mixed fullerene guest molecules (C_{60}/C_{70}) show how the ratio of sorbates of different size can be selectively controlled using applied stress (Fig.2b).

This research demonstrates a means to control the adsorption of guest molecules solely as a function of external pressure. Good control over the variation of pore size with applied stress can be achieved using a high volume change negative Poisson's ratio structure.

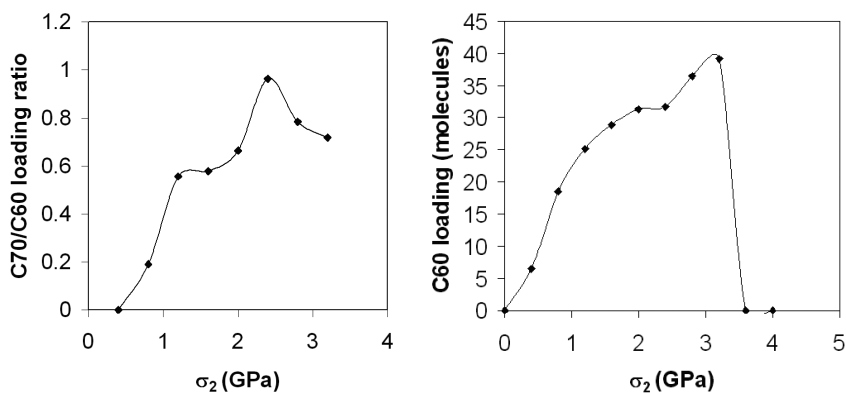


Figure 2. (a) Predicted pressure-dependent loading of C60 in (2,8)-reflexyne; (b) Predicted pressure-dependent loading of C₇₀/C₆₀ in (2,8)-reflexyne

“Modeling enabled a much more cost and time effective approach to be taken to demonstrate proof of concept,” concluded Professor Anderson.

References

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