ELSEVIER

Computational and Theoretical Polymer Science 9 (1999) 335–337

Computational and Theoretical Polymer Science

Numerical search for morphologies providing ultra high elastic stiffness in filled rubbers

A.A. Gusev*, M.G. Rozman[1]

Department of Materials, Institute of Polymers, Universitätsstrasse 6, ETH-Zentrum, 8092 Zürich, Switzerland

Received 5 January 1999; received in revised form 20 April 1999; accepted 20 April 1999

Abstract

We have numerically studied the transverse elastic behavior of a unidirectional composite comprising non-overlapping silica fibers dispersed in a rubber matrix. Some composite morphologies that provided an ultra high transverse shear modulus at rather moderate silica loadings were identified. For these morphologies, predicted elastic stiffening levels were in agreement with those measured at low strains in carbon black and silica filled rubbers, leading one to surmise that such elastic stiffening may also play an important role in the low strain mechanical responses of actual carbon black or silica filled rubbers. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Filled rubbers; Elastic stiffness; Silica fibers

It is the unique combination of stiffness, strength, and abrasion resistance that makes carbon black or silica filled rubbers indispensable today in many demanding applications including tires and engine mountings. At comparably large strain amplitudes, the dynamic properties of filled rubbers are non-linear and strongly depend on the amplitude of the dynamic strain applied, the so-called Payne effect (for an in-depth review and further references, see Ref. [1]). However, at low strain amplitudes the mechanical behavior of filled rubbers become amplitude independent and a remarkable stiffening is observed. For example, at a carbon black or silica volume loading of about 0.3, the low strain shear modulus of a filled rubber is typically about a hundred times larger that of the unfilled rubber [1,2]. Recent experimental results and further references are given in Ref. [2]. Such large stiffening has never been explained with traditional micromechanics-based composite models [3], so a static elastic picture has finally been deemed of little utility for describing the large stiffening observed in filled rubbers at low strains. It is now commonly believed that it is either direct dispersive forces acting between the filler particles [1] or filler induced variations in the topology of the elastic network formed by the rubber chains [4] that are primarily responsible for the unusual stiffening observed.

When dispersed in a rubber, both carbon black and silica particles usually form rather whimsical morphologies with a rich variety of local configurations. For a given filler fraction in a matrix and an arbitrary morphology, it is the variational Hashin–Shtrikman bounds that specify rigorous upper and lower stiffness limits which can never be violated by a macroscopically isotropic elastic composite made up of these two phases [5]. Assuming a bulk modulus of 1 GPa and shear modulus of 0.0005 GPa for the rubber and Young's modulus of 70 GPa and Poisson's ratio of 0.2 for the silica, one readily finds that the Hashin–Shtrikman bounds specify an enormously wide corridor for the overall shear modulus μ. For example, at a silica volume fraction of 0.3 the bounds predict $0.0009 < \mu < 5$ GPa, so even the very high stiffening observed in filled rubbers at low strains does not really violate the Hashin–Shtrikman bounds. This leads one to an interesting question: what morphologies can provide a purely elastic ultra high stiffness similar to that observed in carbon black or silica filled rubbers at low strains?

Here we have numerically identified some elastically ultra stiff morphologies, taking a unidirectional composite as an example. We generated periodic computer models comprising about 50 identical parallel silica fibers dispersed in a rubber matrix (see Fig. 1). An original in-house automatic mesher was used for producing periodic unstructured meshes of about a million triangles. By construction, the meshes accurately reproduced all important features of the composite morphologies studied, including the geometry of thin bridges separating pairs of nearly touching fibers (see Fig. 2). Perfect adhesion was imposed at the interfaces

* Corresponding author. Fax: + 41-1-6321096.

[1] On leave from Institute of Physics, Tartu University, Tartu, Estonia.

1089-3156/99/$ - see front matter
PII: S1089-3156(99)00024-0

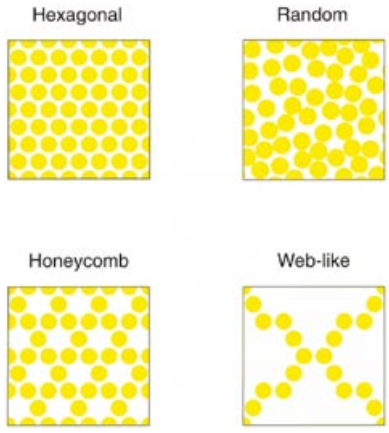
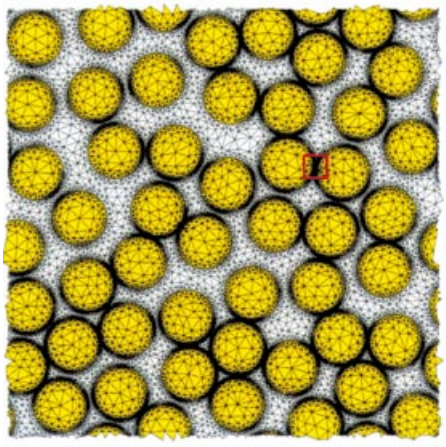


Fig. 1. Sketches of the periodic morphologies studied.



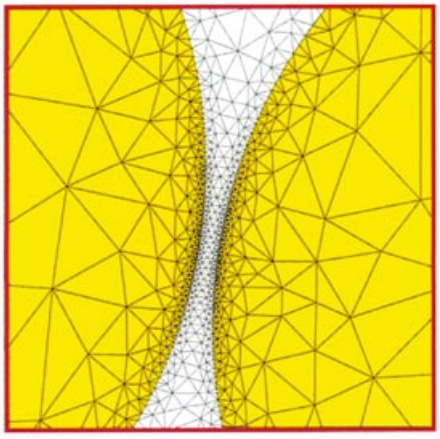


Fig. 2. A periodic unstructured mesh. A small section marked by a red square in the upper fragment is shown magnified in the lower one. The mesh contains a total of about 10^6 triangles. It was found in a separate convergence study that increasing this number did not cause any significant change in the overall elastic behavior.

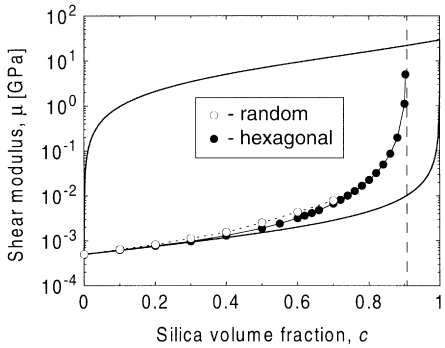


Fig. 3. Numerical results obtained with hexagonal and random packing arrays. The two solid lines give the predictions of the Hashin–Shtrikman variational bounds. The vertical dashed line shows the maximum packing density that can be achieved with identical cylindrical fibers.

between the matrix and inclusions. The size and shape of the periodic computer models were defined by two initially orthogonal continuation vectors **A** and **B**. Overall shear strain was imposed by changing the angle between these two vectors. A conjugate-gradient minimization was employed for finding a set of nodal displacements minimizing the total strain energy. The latter was defined as a sum over the element contributions. The resulting total energy at the minimum gave the overall transverse shear modulus. Further computational details can be found elsewhere [6–8].

Elastic parameters of the phases were taken from the literature. For the rubber matrix, a bulk modulus of 1 GPa and shear modulus of 0.0005 GPa were assumed; while for the silica inclusions Young's modulus of 70 GPa and Poisson's ratio of 0.2 were assumed.

Fig. 3 presents results on the concentration dependence of the overall shear modulus of random and hexagonal packing arrays. It appears that at low silica fractions (say $c < 0.3$) the shear modulus of these two packing arrays have nearly indistinguishable values and their concentration dependence can accurately be described by the lower Hashin–Shtrikman bound. For identical non-overlapping circular fibers, it is the hexagonal packing array that realizes the most dense

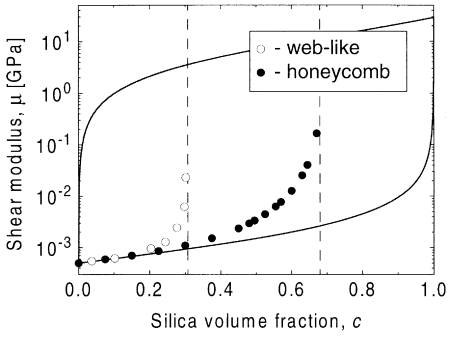


Fig. 4. Numerical results obtained with honeycomb and web-like packing arrays. The two solid lines give the predictions of the Hashin–Shtrikman variational bounds. The vertical dashed lines show the maximum packing density that can be achieved assuming web-like and honeycomb packing arrays of identical cylindrical fibers.

packing possible, i.e. $c_{max} = \pi/(2\sqrt{3}) \approx 0.907$. As the random morphology should unavoidably be converting into the hexagonal one as $c \to c_{max}$, the shear moduli of these two arrays should also become similar. All in all, except for a minor difference at intermediate loadings, the transverse shear moduli of hexagonal and random arrays are quite similar and well below the stiffening levels observed in actual filled rubbers at low strains.

Fig. 3 indicates that the shear modulus of the hexagonal packing array increases sharply as the silica fraction approaches the maximum possible value $c_{max} = 0.907$. To screen the morphologies providing ultra high stiffening levels at lower silica loadings, we studied the elastic behavior of honeycomb and web-like packing arrays (see Fig. 1). For these two arrays, the limiting packing fractions c_{max} are approximately 0.680 and 0.308, respectively. Figs. 3 and 4 indicate that, compared to the hexagonal and random packing arrays, the overall shear moduli of honeycomb and web-like arrays depart from the lower Hashin–Shtrikman bound at much lower silica loadings. In particular, at a silica volume fraction of $c \approx 0.3$ the overall shear modulus of the web-like array studied is already about 100 times larger than that of the unfilled rubber. Interestingly, the same stiffening level is observed in actual filled rubbers at a comparable silica loading [1,2].

To conclude, we have shown numerically that an ultra high elastic stiffening can be realized in a unidirectional composite composed of silica fibers dispersed in a rubber matrix. To achieve this, one should apparently utilize morphologies with nearly touching fibers forming spatially percolating networks. Normally, carbon black or silica particles are more or less spherical, but they are known to form some complex percolating networks when dispersed in a rubber [1]. Realistic studies of the mechanical behavior of periodic three dimensional multi-inclusion models have become feasible only recently [6], so it remains to be seen whether there are some three-dimensional particulate morphologies providing an ultra high elastic stiffening similar to that observed in actual rubbers. It would also be interesting to have more experimental data on the morphology of actual filled rubbers and to see the extent to which the corresponding computer models can exhibit ultra high elastic stiffness.

References

[1] Payne AR, Whittaker RE. Rubber Chem Technol 1971;44:440.
[2] Tse MF, McElrath KO, Wang H-C, Krishnamoorti R, Yurekli K. Paper No. 46, ACS meeting in Nashville, Tennessee, 1998.
[3] Christensen RM. Mechanics of composite materials, New York: Wiley, 1979.
[4] Maier P, Goeritz D. Kautsch Gummi Kunstst 1996;49:18.
[5] Hashin Z, Shtrikman S. J Mech Phys Solids 1963;11:127.
[6] Gusev AA. J Mech Phys Solids 1997;45:1449.
[7] Gusev AA. Bull APS 1999;44:2017.
[8] Gusev AA, Hine PJ, Ward IM. Compos Sci Technol, submitted.