

INTERFACIAL PROPERTIES OF NANOWIRE-POLYMER COMPOSITES

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Summary The mechanical performance of composite materials is critically controlled by the interfacial characteristics of the reinforcing phase and the matrix material. Here we report a study on the interfacial properties of a silicon nanowire-reinforced polystyrene nanocomposite system through molecular mechanics simulations. Results of a nanowire pullout simulation suggest that the interfacial shear transfer stress of this novel system is significantly higher than for many traditional fiber reinforced composite systems.

INTRODUCTION

Nanocomposites are a new class of composites, that are particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range. Three types of nanocomposites can be distinguished, depending on how many dimensions of the dispersed phase are in the nanometer scale. When the three dimensions are in the order of nanometers, we are dealing with isodimensional nanoparticles such as spherical silica and aluminium nanoparticles or semiconductor nanoclusters. When two dimensions are in the nanometer scale and the third is larger, forming an elongated structure, we speak about nanotubes or nanowires. Finally, the third type of nanocomposites is characterized by only one dimension in the nanometer range. In this case the filler is present in the form of sheets of a few nanometers thickness and up to one micrometer long. This family of nanocomposites, known as polymer-layered crystal nanocomposites, is almost exclusively obtained by the intercalation of the polymer inside the galleries of layered host crystals. There exist a wide variety of both synthetic and natural crystalline fillers, which are able, under specific conditions, to intercalate a polymer. Polymer-layered crystal nanocomposites are now commercially available and have been throughout investigated in a large amount of publications during last ten years.

Nanocomposites with elongated structural fillers have recently attracted many investigations. A focus is exclusively on nanocomposites with carbon nanotubes due to carbon nanotubes unique physical properties, including mechanical, thermal, optical and electrical. However, after nearly a decade of research, their potential as reinforcement for polymers has not been fully realized; the mechanical properties of derived composites have fallen short of expectations. Yet, given the magnitude of the carbon nanotubes mechanical properties, strength as high as 200 GPa and elastic moduli close to 1 TPa range, significant improvement on current composites should be possible provided means to harness the nanotubes unique attributes exhibited at nanoscale can be transferred to the macroscale. Since these excellent mechanical properties of carbon nanotubes cannot as yet to be utilized to a full extent (not mentioning their high price), seeking an alternative seems to be well motivated. Nanowires, having a diameter comparable to carbon nanotubes, aspect ratio close or above 10^3 and a few hundred times more surface area per volume than a classical fiber reinforcement, may be considered as a new family of a reinforcing phase for nanocomposites, and their study will constitute the main object of this contribution.

Silicon-based nanotubes and nanowires

Carbon nanotubes have been providing increasing challenges for silicon in the field of nanotechnology. Since silicon-based materials have been the focus of extensive research due to their technological importance, new forms of stable silicon nano-structures are required to sustain the current silicon-based technology and as a by-product it might bring benefits to the field of structural nanocomposites. Unlike carbon nanotubes, no silicon nanotube has been yet observed experimentally. However, an intensive theoretical work has been done, exploring the possibility of the existence of silicon nanotubes and similarities with carbon nanotubes regarding their structural and electronic properties have been found. It is well known that carbon and silicon possess different bonding capabilities, despite the fact that they belong to the same group of the periodic table. Nevertheless, the partial substitution of carbon with silicon atoms was achieved and the first experimental synthesis of hetero-nanotubes was performed in 2001 resulting in 50% silicon-50% carbon nanotubes.

As opposite to hypothetically possible silicon nanotubes, the knowledge and technology of silicon nanowires is well advanced. Silicon has long been synonymous with semiconductor technology. This role is due largely to the remarkable properties of the silicon-silicon dioxide interface, which covers bulk crystalline core of the nanowires. The technology is also available to remove the silicon-dioxide shield to obtain pure silicon nanowires. The fabrication of silicon nanowires with diameters ranged from 1.3 to 190 nm, growing rate up to the order of 8 micrometers per minute and length of a few micrometers is now well established.

NANOWIRE-POLYMER INTERFACE

A number of micromechanical calculations have been performed to predict behaviour of composite interfaces, showing that the detailed behaviour of the material at these interfaces frequently dominates the behaviour of the composite as a

whole. In order to calculate mechanical properties of specific interfaces an atomistic model is necessary. We choose to study the behaviour of an interface in a silicon nanowire/polystyrene matrix nanocomposite. Adhesion strength between two phases was studied using a molecular mechanics model shown in Fig. 1. The polystyrene chain has been pulled away from the silicon-silicon dioxide sheet, and the energy of the system at specified distances between the two was calculated.

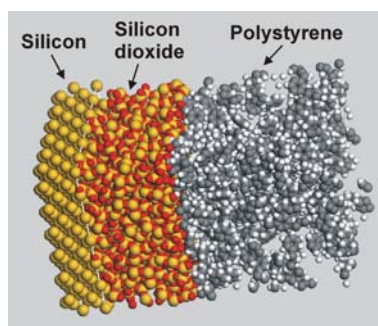


Figure 1

culated. The adhesion energy is calculated as the difference between the minimum energy and the energy at infinite separation. It has been shown that the adhesion energy depends on the length of polystyrene chains. The nature of this adhesion energy comes from electrostatic and van der Waal's forces. For the nanowire totally embedded in the polymer matrix an additional interaction is present due to constrained deformation of the nanowire.

A single nanowire composite model was constructed with either a pure silicon core or a wire having also the silicon dioxide shield. A former case is depicted in Fig. 2, where a front view (a) and configuration before a pullout (b) are illustrated. Nanowire pullout simulations were performed after carrying out optimisation procedures for energy minimization of the system and pulling out the nanowire with predetermined displacement intervals, Fig. 2c. The energy

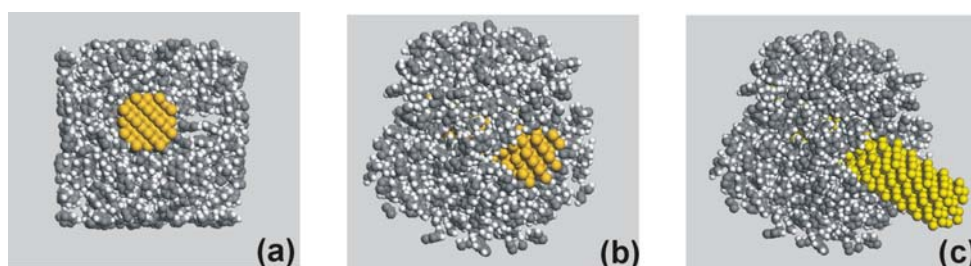


Figure 2

difference between the fully embedded nanowire and the complete pullout configuration is the work required for nanowire pullout. Inclusion-matrix interfacial shear stress is a critical parameter controlling the efficiency of stress transfer and hence important properties of composites. The interfacial shear stress is derived from the total work done during pulling the nanowire from the polymer matrix and is about 150 MPa, which is about one order of magnitude higher than many fiber reinforced composites. The calculated interfacial shear stress is based on an average shear stress assumption. Determination of the shear stress distribution would necessitate a detailed analysis of individual chain displacements during pullout in a vicinity of the nanowire, which is computationally very demanding task.

CONCLUSION

A novel silicon nanowire-polystyrene nanocomposite has been investigated using molecular mechanics simulations with respect to interfacial characteristics of the system. The adhesion energy and the interfacial shear stress has been determined indicating significant bonding quality as compared with traditional fiber reinforced composite systems. Further improvement of the shear stress transfer could be achieved with functionalization of silicon nanowires with coupling agents.

An extended molecular simulation study should consider influence of nanowire geometry such as critical aspect ratio and diameter on interfacial stress distribution, both of which are shown to affect stress transfer behaviour. Furthermore, an immobilization of polymer chains in a vicinity of nanowires should be investigated in order to determine an effective domain of reinforcement of the polymeric matrix. All these factors may serve as an input for micromechanical modelling of nanocomposites at micrometer length scale and subsequently at a continuum level for the determination of effective bulk properties.