

# MODELLING POLYMER NANOCOMPOSITES WITH FUNCTIONAL NANOWIRES

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## 1 Introduction

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 [1-3].

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 classical fiber reinforcement, may be considered as a new family of a reinforcing phase for nanocomposites.

Being one of the most important functional semiconductor materials, ZnO has been widely applied in the opto-electronic industry because of its excellent optical (high fluorescence yield in the UV and green), electrical and piezoelectrical properties [4]. The one-dimensional nature of nanowires means that strain in the surrounding polymer matrix is easily detected in the anisotropic fluorescence from the composite. Therefore, highly fluorescent ZnO nanowires can be applied for *in situ* monitoring of strain. Hence, a careful selection of nanostructured elements embedded in the host polymer may incorporate multifunctionality into

nanocomposite materials, which would not be achievable otherwise.

The aim of present investigation is to perform molecular dynamics simulation of polypropylene/ZnO nanowires nanocomposites in order to predict their mechanical and optical properties.

## 2 Structure of ZnO nanowires and composites

Zinc oxide nanowire grow in a wurtzite structure and they typically form with a hexagonal cross section having the c-axis along the direction of the wire. Figure 1 illustrates a stable ZnO structure.

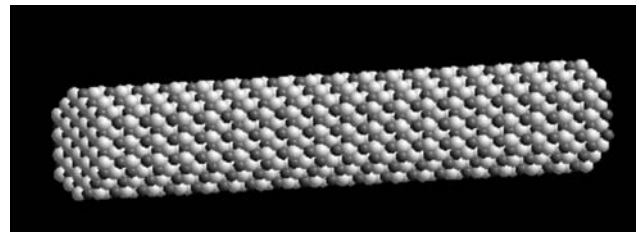


Fig. 1. Stable structure of ZnO nanowire.

All dangling bonds on the nanowire surfaces were saturated by means of hydrogen atoms not shown in the figure. The nanowire has been subjected to stepwise elongation along its axis for the prediction of axial stiffness and failure. Equilibration and energy minimization has been performed after each deformation step. Changes in photoluminescence bands have been recorded during entire deformation process indicating sensing properties of nanowires. All structural calculations of nanowires have been performed using PM3 semi-empirical method implemented in commercially available package HyperChem<sup>®</sup>.

A single zinc oxide nanowire-polypropylene model was constructed. Nanowires were placed in the cavity of a polymeric network and subject to energy minimization in order to obtain a reference

configuration. The energy minimization was carried out employing molecular mechanics MM+ code from the same software package. Nanowire pullout simulations were performed consisting of number predetermined deformation steps, where a fully embedded nanowire was being “pulled” out from the polypropylene matrix. After each step, the energy minimization was performed and energy of the nanowire has been recorded. Then interfacial shear stresses can be calculated from the energy difference between the fully embedded nanowire and the complete pullout configuration which is equal to the work required for nanowire pullout.

### 3 Atomistic deformation analysis

The most frequently used form for the stress at atomic level is based upon the Clausius virial theorem, which determines the stress field applied to the surface of a fixed volume containing interacting particles (atoms). The virial stress includes the mass and velocity of atoms, which describes the fact that mass transfer causes mechanical stress to be applied on the surfaces external to an atomic system, as well as it includes pair-wise interatomic forces and atomic positions. It has been shown that the virial stress cannot be directly related to the classical Cauchy stress and several modifications have been proposed [5, 6]. It is essential to recognize that the stress at the location of an atom depends on the details of the interatomic interactions and the positions of interacting neighbours. Hence, the atomic stress is a non-local function of the state of the matter at all points in some vicinity of the reference atom, in contrast to the local stress field used in classical continuum theories.

It seems that the relationship between local displacements of atoms and the strain tensor is not ambiguous as the concept of atomic stress [7, 8]. Position of atoms is readily available from almost all molecular simulation algorithms and the atom displacement can be easily assessed. The atomic strain will be defined in terms of Voronoi tessellation. The atoms are assumed to be in their equilibrium positions, and thermal vibrations are averaged. The Voronoi polyhedron around central atom is composed of a set of sub-polyhedrons (interaction cells) whose number is determined by a number of neighbours to the central atom. During motion, the Voronoi polyhedron associated with the atom changes its shape. The interaction cell is defined for each pair consisted of a central

atom and its neighbors. It is a part of Voronoi polyhedron that contains points situated closer to this pair of points than to any other. It is build of two sub-polyhedrons (parts of polyhedron surrounding a central point and a neighboring point) having common face. This is a unique region for which it can be assumed that it is influenced only by these points. Strain measure is a relative quantity and one need two configurations, the reference and the present, in order to define the local atomic strain during deformation.

An atomic strain tensor was obtained from the deformation gradient tensor that provides the best mapping of the present and reference configurations. It was concluded that local atomic strain for nanowire atoms follows the overall deformation of the nanocomposite until a certain deformation threshold has been reached. The atomic strain concept allows analyzing the molecular structure atom by atom, which may give a unique insight into deformation phenomena operative at molecular level such as interface behaviour in nanocomposites

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