Soft engineering at the nano-scale

Rachel Yerushalmi – Rozen

Self-assembly in hybrid systems of nanostructures surfactants and polymers

Control of the structure and properties of nanometric assemblies offers new possibilities for the engineering of materials with desired properties. The desired control over the behavior of molecular assemblies may be achieved by chemical or physical means which result in induced steric confinement, manipulation of interfacial forces or modification of the correlation lengths.

An ultimate strategy for preparation of functional nano-structured materials are self-assembly (SA) and engineered assembly of multi-component structures. Over the last few years we have investigated the self assembly in polymers-nanoparticles systems (BSF 2007-2011), carbon-nanotubes-induced assembly of surfactant molecules into liquid-crystalline –like structures (ISF 2009 -2013), and polymer-carbon-nanotubes interactions (ISF 2006-2009).

Polymers and carbon-nanotubes: In a detailed experimental investigation, carried out in collaboration with Prof. Daniella Goldfrab from the Weizmann Institute, Israel, we combined thermal measurements and spin-probe electron paramagnetic resonance (EPR) to map the behavior of a hybrid system comprising of carbon nanotubes and self-assembling polymers in aqueous media. Novel hybrid structures and unique behaviors were observed due to coupling between the components. The degree of coupling was found to depend on the size-matching between the diameter of the native micelles and the nano-structures. The study highlights the role of dimensionality in combined assembly of polymers and nano-structures and offers new possibilities for the engineering of nano-structured materials.

Surfactants and carbon-nanotubes: In collaboration with Prof. Oren Regev and Prof. Moshe Gottlieb from the department of Chemical Engineering at BGU, we found that minute amounts of dispersed single walled carbon nanotubes (SWNT) may lead to the formation of ordered micellar arrays over mesoscopic length scales in thin films of surfactant solutions. The effect is unique to SWNT and is not observed with other additives. In addition, we found that the presence of SWNT results in a significant increase in the low shear-rate viscosity and shear thinning replacing Newtonian behavior. We suggested that SWNT may induce the formation of size-matched elongated surfactant micelles that further orient under the action of external shear. A similar effect was not observed in dispersions of multi-walled carbon nanotubes or carbon black particles, suggesting that the cooperative behavior is not invoked when significant size-mismatch exists between the surfactant micelles and additives.



Fig. 2 Miniscule amounts of dispersed single-walled carbon nanotubes induce the formation of elongated micelles, modify the phase behavior, and alter the rheological characteristics of surfactant solutions. The Cryo-TEM image (*IKI microscopy unit*) shows about half micronlong cylindrical micelles, oriented parallel to individual SWNTs (darker lines)

Towards engineering of the carbon nanotube- conjugated polymer interface

In collaboration with G. Frey (Technion), J. Frey (Bar Ilan University) and E. Katz from the IKI we are investigating different aspects of carbon-nanotubes based photovoltaics (Bikura 2007-2010). The aim of this interdisciplinary project is to offer a new paradigm for designing the conjugated polymer/CNT interface towards the fabrication of high-efficiency organic solar cells. Both chemical interactions at the polymer/CNT interface and enhanced electron transfer at the polymer- CNT interface are investigated. The first stage of the project has been completed successfully with the design and synthesis of block-copolymers that are able to incorporate SWNT into the matrix of conjugated polymers. (JPC C 2010). The second stage of the project involves studies of quenching of the photoluminescence and electron transfer (as measured via light-induced ESR) at the crbon-nanotube polymer interface.



Fig. 3 Images of P3HT-PCBM-**SWNT** fibers prepared via electrospinning following the procedure described in the text. (a) Optical image of fibers collected on glass (b) SEM image of a fiber. (c) Absorption of P3HT films (blue, 300 nm) and fibers (red) prepared from a solution of P3HT - PEO in anhydrous chloroform. (d) Scanning Probe Microscopy (SPM) image taken in torsional resonance, a non-contact technique, of fibers collected onto a silicon wafer. (Poly. Phys B 2011).