

CARBON NANOTUBE ENGENDERED POLYMER ORGANIZATION

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CARBON NANOTUBE ENGENDERED POLYMER ORGANIZATION

by
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DEPARTMENT OF CHEMICAL ENGINEERING

Submitted

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Certificate

This is to certify that the thesis entitled “**Carbon Nano-tube Engendered Polymer Organization**” being submitted by **Mr. Sunil Kumar** to the Department of Chemical Engineering, **Indian Institute of Technology Delhi** for the award of the degree of **DOCTOR OF PHILOSOPHY**, is the record of the bonafide research work carried out by him under my supervision and guidance. The work presented in this thesis have not been submitted either in part or in full to any other university or institute for the award of any degree or diploma.

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Abstract

The properties of single-wall carbon nano-tubes (SWCNTs)-polymer composite are highly influenced by the polymer chain's organization. Despite many experimental and theoretical studies, the understanding of the polymer chain organization near the interface at the atomic scale is far from complete. The reason for the lack of understanding is due to the complex organization of polymer near and far from the surface of the SWCNT.

We have used molecular dynamics simulations to study the organization of semiflexible polymer chains near SWCNT at different values of polymer chain stiffness, radius of SWCNT and temperature profiles. We have taken the system at very high temperature and cooled to a desired temperature by quenching or stepwise cooling.

In the quenching, the beads of the polymer chain organize in lamella-like patterns on the surface of the SWCNT with the long axis of the lamella parallel to the axis of the SWCNT. In the stepwise cooling process, the polymer beads form a helical pattern on the surface of a relatively thick SWCNT but form a lamella-like pattern on the surface of a very thin SWCNT. We carried out (thermodynamical equilibrium) free energy calculations for these two chain arrangements. These calculations have shown that the free energy for the helical wrapping is smaller than for a lamella conformation for all nano-tubes except the most narrow. The preference of helical wrapping for the stepwise cooling process is probably due to large number of trans conformations within the polymer chain. The free energy calculations also predicted the pitch of the helix is always quite large (between 60° and 80°). This prediction is in correlation with the MD simulation results. The free energy calculations lead to minimum free energy states corresponding to a particular chain being given sufficient opportunity to investigate many different chain conformations. This corresponds to step-wise cooling. However, in direct cooling

the chain often gets trapped in a metastable state. The more probable (but not necessarily the lowest free energy state) chain conformation is a hairpin (during a sudden quench).

Due to the different curvature inside the SWCNT to outside, there are increased numbers of polymer-SWCNT bead contacts for polymers which reside inside the SWCNT. A sufficiently long polymer chain first adsorbs on the exterior of the SWCNT and subsequently moves inside the cavity of the SWCNT. At equilibrium, the polymer configuration consists of a central stem surrounded by helically wrapped layers inside the nanotube. Sections of the polymer outside the SWCNT have helical conformations (for SWCNTs of small radius) or circular arrangements (for SWCNTs of larger radius). Polymers encapsulated within the SWCNT have an increased chirality due to packing of the beads and this chirality is further enhanced for moderately stiff chains.

We have explored the effect of the organizations of semi-flexible polymer on mechanical properties such as elastic modulus and yield stress of the polymer-SWCNT composite. The proportions of locally ordered organization of polymer chains in a sample depend on its flexibility. For a fixed flexibility of a polymer chain, the presence of SWCNTs improves the proportion of regularly arranged polymers present in the composite. In turn, this improves the elastic modulus and yield stress of the polymer of higher rigidity. The enhancement in elastic modulus and yield stress is due to the retarded deformation of densely packed, ordered region of polymer chains in polymer/SWCNT composite. The presence of randomly oriented chains in a polymer sample containing regularly arranged polymer leads to the higher strain at yield point.

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