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Reseach Article

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Type and Size Selectivity of Single-Walled Carbon Nanotubes by Phenylethynyl Terminated Imide Oligomers

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Abstract

Aromatic polyimides are well-known as high-performance polymer materials which have excellent properties such as high thermal stability, strong mechanical strength, and superior chemical resistance. However, rigid backbones of oligomers and strong chain interactions result in lower processibility. Our molecular modeling suggests that the enhancement of nanotube solubilization is attributed to the formation of self-assembled intermolecular structures associated with the inclusion of curing agents, in conformity with experimental findings. On the other hand, isolation of single-walled carbon nanotubes (SWNTs) with specific chirality and diameter is critical for achieving optimum performances of SWNTs in various application. Our studies reveal that phenylethynyl terminated imide (PETi) oligomer selectively enriches metallic and semiconducting (6, 5) SWNT.

Introduction

Single-walled carbon nanotubes are attractive materials due to their intrinsic electronic, mechanical and transport properties. SWNTs can be made by wrapping a graphene sheet [1]. Most of the properties of SWNTs change significantly with the chirality. In particular, their band gap can vary from zero to about 2 eV and their electrical conductivity can show metallic or semiconducting behaviour [2-4]. Due to this reason, SWNTs are likely candidates for miniaturizing electronics [5-13]. In contrast to the excellent properties, SWNTs typically exist in the aggregate form. Tubes of different properties are held together due to the strong π-π interaction among the tubes. The aggregation prevents the optimum performances of SWNTs.

On the other hand, aromatic polyimides are well known as high-performance polymer materials widely used in aerospace and electronics fields. They have some excellent chemical, mechanical and thermal properties [14]. However, the rigid backbones of polyimides and strong chain interactions result in weak solubility and high softening or melting temperature for most of the aromatic polyimides. Inadequate solubility and high melting temperatures limit the uses of polyimides for commercial purposes. Recent research has developed several polyimides from various aromatic diamines and dianhydrides that can be melted processed into coatings, adhesives, composites and films. Controlled molecular weight imide oligomers containing phenylethynyl groups [phenylethynyl terminated imide (PETi), e.g. PETi-8, PETi-330] have exhibited exceptional processability during fabrication of neat resin moldings, bonded panels and composites, albeit typically under 2.4 MPa (200 psi) [15-17]. Combination of these two make an excellent composite which has unique properties of both SWNTs and PETi 330. Apart from that PETi 330 disperse carbon nanotubes and shows a selectivity towards some of the nanotubes. This allows us to isolate the desired SWNTs which have the required properties.

In recent years there has been considerable interest in incorporating nanomaterials into polymeric matrix composites (PMCs) to modify mechanical, thermal, and electrical properties, thermo-oxidative stability and moisture absorption [18]. Aromatic phenylethynyl-terminated imide (PETi) resins, a mixture of low molecular weight oligomers with phenylethynyl end caps, have been designed that upon heating, melt to give a low viscosity melt. The mixture of low molecular weight oligomers which upon further heating undergo chain elongation and cross-linking to give high performance polyimides with high glass transition temperatures. Ghose and co-workers have incorporated carbon nanotubes into PMCs by melt mixing the nanotubes into PETi resins via ball milling followed by fabrication by resin transfer molding (RTM) [19]. The Recent experimental study has shown that multi-walled carbon nanotubes (MWCNTs) can be effectively dispersed in PETi resin by high torque melt mixing and processed into polymer matrix composites with improved electrical conductivity, mechanical properties, and

resistance to moisture adsorption.

The anhydride moieties in the 3,3, 4,4-biphenyltetracarboxylic dianhydride (BPDA) and 4- phenylethynylphthalic anhydride (PEPA) molecules play a role as electron acceptor and the diamine moieties in the 1,3-bis(3-aminophenoxy)benzene (APB) and 3,4-oxydianilien (ODA) molecules as the electron donor [20]. Under high torque melt mixing that PETi wets out and bundles MWCNTs, and these resin MWCNTs mixtures can be processed into high quality composites by RTM

Method

Computational calculations were based on Materials Studio 5.5 [21] and TeraChem 1.0 packages [22, 23]. PETi-298 and PETi-298/SWNTs were optimized using with triple numerical polarized (TNP) basis functions and empirical dispersion corrected density-functional approaches [21]. Electronic properties of different conformations were investigated using dispersion-corrected first-principles density-functional calculations. We used the Perdew-Burke-Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA). Tkatchenko-Scheffler (TS) dispersion correction accounts for the relative variation in dispersion coefficients of differently bonded atoms by weighting values taken from the high-quality ab-initio database with atomic volumes derived from partitioning the self-consistent electronic density. The inclusion of dispersion-correction in the calculation enable to study the non-covalent π-π interaction between the PETi-298 and SWNTs.

Results

Imide oligomers are step or condensation oligomers derived from both aliphatic or aromatic dianhydrides and diamines, or their derivatives, and contain a heterocyclic imide linkage in the repeat unit.

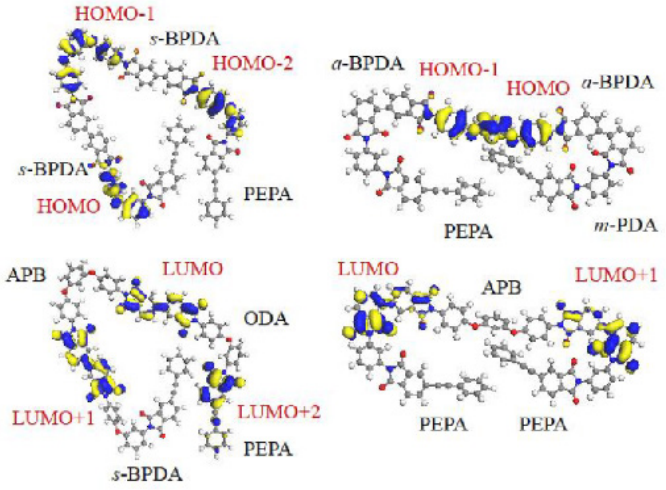

Figure 1: Optimized structure of PETi-298 along with the calculated charge distribution of unoccupied and occupied molecular levels.

The molecular and chemical structure of PETi-298 is shown in Figure 1. PETi-298 was modelled and the structure was geometrically optimized by using DMol3 [21]. Molecular orbitals were calculated to identify the donor-acceptor interaction between moieties of PETi-298 (Figure 1). In the PETi chain, the anhydride moieties in the BPDA and PEPA molecules play a role as an electron acceptor and the diamine moieties in the APB and ODA molecules as the electron donor [20]. Electron-donor and acceptor molecules can intermolecularly interact with each other forming the complexes depending on the molecular environment between two neighbouring molecules in the different imide chains during the imidization process.

To explore the nature at the molecular level of nano-reinforced composites, we planned to carry out detailed molecular dynamics simulations for the interaction of SWNTs with PETi. The calculations were based on intensive geometry optimization studies of conformations via force-field based molecular dynamics. Whereas our preliminary molecular dynamics simulation confirms that the PETi oligomer self-assembles onto the surface of the SWNTs, the uncured and cured state of PETi oligomer adopts energetically favourable configurations by wrapping around the tube helically.

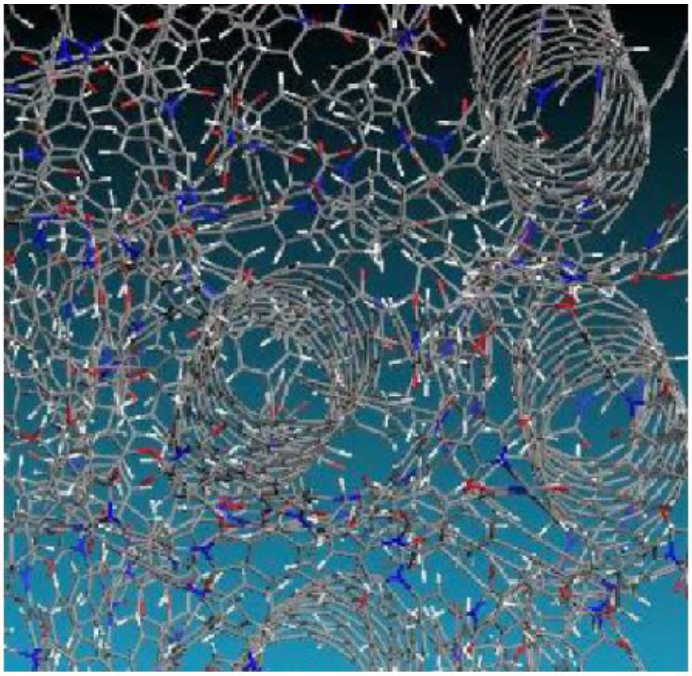

Figure 2: Annealed structure of 10 PETi-330 monomer chains and 2 PETi-wrapped tubes in a box corresponding to a density of 1.36 g/cc.

Illustrated in Figure 2 are optimized structures of SWNT wrapped with chain-like PETi resin. A careful examination of the dynamical structural and energetic changes reveals that electrostatic interactions within the PETi backbone are primarily responsible for wrapping into a helical structure. The aromatic rings in the PETi resin are planer to the surface of the SWNT, and the structural changes proceed through a rearrangement of the torsion angles. As seen in Figure 2, the optimized structure tends to align the backbone along the nanotube surface in order to maximize the interaction between π-bonds, triple C-C bonds, and aromatic rings. The backbone torsion in helix formation is important for the cured resin to wrap successfully around the tube. Furthermore, as the binding of conjugated polymers is the combination of electrostatic and ven der Waals (vdW) interactions, the binding is stronger than vdW binding on nonconjugated oglimers, which is expected to yield improved dispersion in conjugated polymers [22-24].

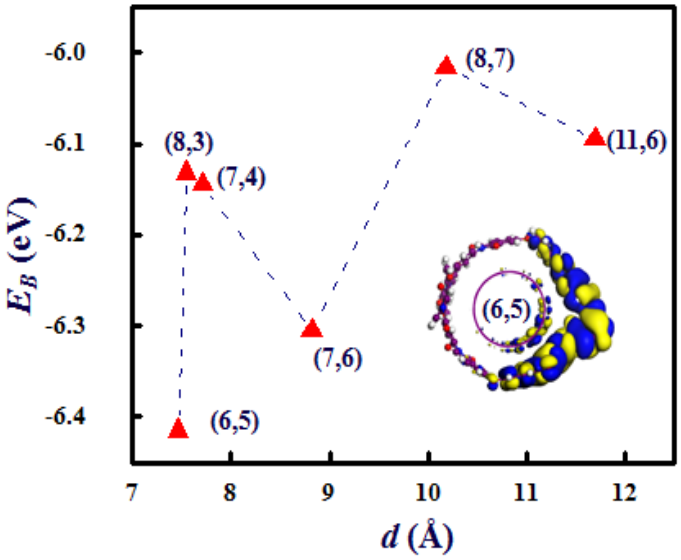

Figure 3: Extracted Binding energy of various SWNTs. Inset: charge density plot of semiconducting (6,5) SWNT with PETi

The capability of forming a helical conformation for imide oligomer or polyimide resins has important ramifications in dispersing nanotubes [25]. Our molecular modelling suggests that the enhancement of nanotube solubilisation can be attributed to the formation of self-assembled intermolecular structures associated with the inclusion of curing agents. The results are also in conformity with the experimental findings that the polyimide resins exhibit higher fracture toughness and improved mechanical properties as compared to uncured resins.

In order to shed some light on the dispersion selectivity, the computational study was carried out by using dispersion-corrected DFTB method [21]. To examine the polymer's affinity to different SWNTs, dispersion-corrected DFTB method was employed to gain further insight into the interaction between the phenylethynyl terminated imide (PETi) 330 and various SWNTs. The binding energy (Figure 3) was calculated from density functional tight binding method (DFTB). To calculate the binding energy, we have used the following formula: E = EPETi/SWNT - ESWNT – EPETi, where EPETi/SWNT is the total energy of the composite, ESWNT is the energy of the nanotube without PETi 330, and EPETi is the energy of the PETi 330 without the nanotube. In other words, the binding energy can be calculated as the difference between the energy of optimized composite structure and the energy of separated nanotube and PETi 330.

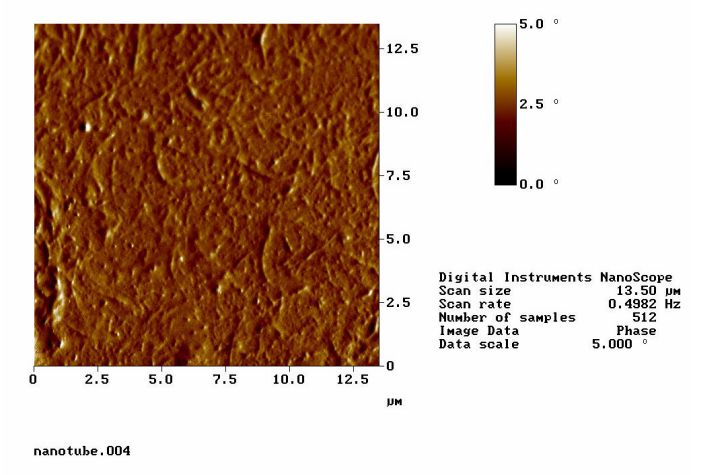

Figure 4: AFM image obtained in tapping mode. The image is shown in the height (left) and the phase (right) modes.

The dispersion of SWNTs in PETi-298 was studied experimentally. In a typical procedure for nanotube dispersion, 3 mg of SWNTs sample were dispersed by using 5 mg of oligomer in 20 mL chloroform. The solution was sonicated at 0oC for one and half hours, followed by centrifugation at 7000 rpm for one hours to remove the sediment of the undispersed SWNTs. In order to further remove the catalyst metal SWNTs, [1] the supernatant solution was further centrifuged at 20000 rpm for two hours. The resulting supernatant solution of SWNT/PETi oligomer in chloroform was stable for several weeks. Aggregation of SWNTs could be observed after setting the supernatant solution for several weeks at room temperature.

A thin film of SWNT/PETi oligomer was prepared by spin-casting the supernatant solution on a silicon wafer substrate. An atomic force microscopy (AFM) image of the SWNT/PETi (Figure 4) revealed that SWNTs were dispersed as single tubes in PETi oligomers. The length of SWNT is around 1~2 μm, however the wrapping mode is not clear to see because of the resolution of AFM image.

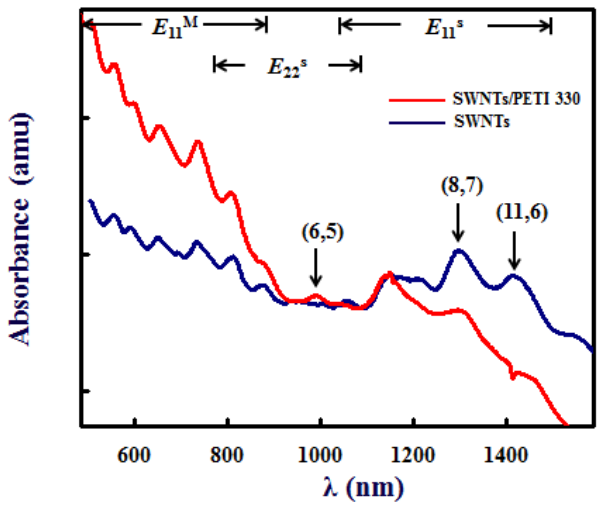

Figure 5: UV-vis absorption spectra of dispersed SWNTs (in water) and SWNTs/PETi supernatant solution (in chloroform).

As seen in Figure 5 the UV-vis absorption spectra revealed that metallic SWNTs carbon nanotubes were enriched by oligomer wrapping, as the absorption in the metallic region became significantly higher [26]. In sharp contrast, majority semiconducting SWNTs were decreased after dispersion by PETi oligomer. Notably, the absorption of the semiconducting (6,5) SWNT (λmax at ~992 nm) was increased. The results thus point to that the PETi oligomer can selectively disperse the metallic SWNT, as well as the semiconducting (6,5) SWNT.

The intriguing selectivity to (6,5) SWNT was further evidenced in the 2D photoluminescence (PL) of SWNT samples (Figure 6). In the raw SWNTs, the signal of (6,5) was weaker than that of (7,5) and (8,4) SWNTs (Figure 6a). After dispersion with PETi oligomer, the PL signal from (6,5) SWNT became the strongest one (Figure 6b), in comparison to the other semiconducting SWNTs. The overall weak PL signals SWNT/PETi sample were attributed to the presence of enriched metallic tubes which are known to quench the fluorescence.2 In comparison with raw SWNTs, the major emission signals were red-shift by about 10-20 nm in the spectrum of SWNTs/PETi, which indicates strong interaction between SWNT and PETi oligomer. These results agree with the molecular dynamics studies on oligomer wrapping.

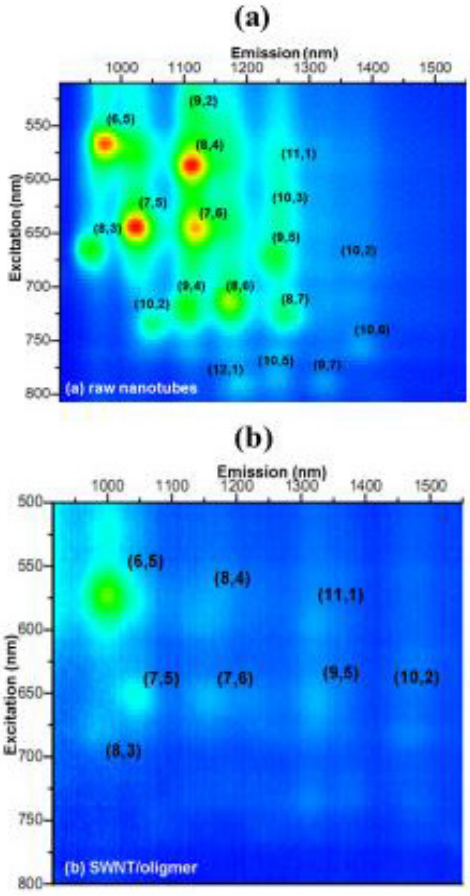

Figure 6: 2D photoluminescence (PL) of SWNT samples. (a) Raw SWNTs were dispersed with sodium dodecylbenzene sulfonate (SDBS) surfactant. (b) SWNTs/PETi-330 were dispersed in chloroform.

In summary, PETi oligomer selectively enriches the metallic SWNTs. Among at least 17 semiconducting SWNTs existed in the raw sample, PETi also selectively enriches the semiconducting (6,5) SWNT, which has a smaller diameter (d=0.757 nm). Computational studies including molecular dynamics and dispersion corrected DFT calculations confirms the experimental findings. The selectivity towards semiconducting (6,5) SWNT is due to the strong binding between the nanotube and the PETi-298 oligomer. The observed stronger binding may be due to the π-π interaction between the polymer and the SWNT.

Acknowledgement

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