Noncovalent Engineering of Carbon Nanotube Surfaces

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ABSTRACT

We report here that the rich functional chemistry of poly(aryleneethynylene)s (such as PPE) allows us to prepare various single-walled carbon nanotubes (SWNTs) with tunable functionalities and solubilities. In contrast to pristine SWNTs, soluble SWNTs can be homogeneously dispersed in commercial polymers such as polycarbonate, polystyrene etc. These composites showed dramatic improvements in the electrical conductivity and mechanical properties.

Keywords: carbon nanotubes, chemical functionalization, dissolution, composites

1 INTRODUCTION

Single-walled carbon nanotubes (SWNTs), due to their novel structural, thermal, electrical, mechanical and optical properties, are expected to find applications in many fields. In order to take advantage of the full potential of SWNTs, it’s necessary to address the fundamental issues (cutting, solubilization, chemical functionalization, purification, manipulation, and assembly) in molecular engineering of carbon nanotubes.1-14 Pristine SWNTs are generally insoluble in common solvents, and difficult to functionalize controllably. We recently reported a non-wrapping approach to noncovalent engineering of carbon nanotube surfaces by short, rigid functional conjugated polymers, poly(aryleneethynylene)s (PPE). This method enables the superior control of the relative placement of functionalities on the nanotube surface while still preserving nearly all of the nanotube’s intrinsic properties.15

Short, rigid conjugated polymers, poly(aryleneethynylene)s (such as PPE),16 are used to solubilize SWNTs. In contrast to previous work,17-19 the rigid backbone of PPE cannot wrap around the SWNTs. The major interaction between polymer backbone and nanotube surface is most likely π-stacking (Figure 1).20 This approach allows control over the distance between functional groups on the carbon nanotube surface, through variation of the polymer backbone and side chains. This approach represents the first example of carbon nanotube solubilization via π-stacking without polymer wrapping and enables the introduction of various neutral and ionic functional groups onto the carbon nanotube surface.

Figure 1. A molecular model of PPE-SWNT complex.15

2 RESULTS AND DISCUSSION

We report here that the rich functional chemistry of PPE allows us to prepare various functional SWNTs with tunable functionalities. The PPE-functionalized SWNTs can be solubilized in various organic solvents and water, and the solubilities are as high as 10 mg/ml. The soluble SWNTs with specific functionalities can be used as novel gelators that can gelate various organic solvents such as chloroform, 1-methyl-2-pyrrolidinone etc.21,22

Two common approaches have been used previously to disperse the SWNTs in a host polymer: 1) Dispersing the SWNTs in a polymer solution by lengthy sonication (up to 48 h).23 The lengthy sonication, however, can damage/cut the SWNTs, which is undesirable for many applications. 2) In situ polymerization in the presence of SWNTs.24,25 The efficiency of this approach, however, is highly dependent on the specific polymer. For example, it works better for polyimide24 than polystyrene25.

Our noncovalent chemistry can provide nanotube solubilization in organic solvents that allows homogeneous dispersion of nanotubes in the host polymer matrix. This approach avoids the lengthy sonication and is applicable to many organic soluble polymers such as polycarbonate, polystyrene and poly(methyl methacrylate) etc.26

Homogeneous nanotube polymer composites can be fabricated using noncovalently functionalized, soluble SWNTs (Figure 2.), and these composites show dramatic improvements in electrical conductivity with low percolation threshold (0.05-0.1 wt% of SWNT loading).26 By significantly improving the dispersion of SWNTs in commercial polymers, we show that only a very small
amount of SWNTs are needed to achieve conductivity levels required for different electrical applications without compromising the host polymer’s other desired physical properties and processability (Figure 3 and 4). The electrically conductive CNT polymer composites will find various applications such as electrostatic dissipation, EMI shielding, printable circuit wiring, and transparent conductive coatings.

The SEM images of the surface and cross-section of PPE-SWNTs (5 wt% of SWNTs)/polystyrene composite film show the excellent dispersion of PPE-functionalized SWNTs in host polymer matrix. SWNTs are randomly distributed not only along the surface (Figure. 2a), but also through the cross section (Figure. 2b and 2c), indicating the formation of an isotropic, three-dimensional nanotube network in host polymer matrix. This is essential for obtaining composites with isotropic electrical conductivity.

Figure 3a shows the measured volume conductivity (using the standard four-point probe method) of PPE-SWNTs/Polystyrene composites as a function of the SWNT loading. The conductivity of pure polystyrene is about $10^{-14}$ S/m.

Figure 3b indicates an extremely low percolation threshold at 0.045 wt% of SWNT loading. The very low percolation threshold is a signature of excellent dispersion of high aspect ratio soluble SWNTs.

Apart from the very low percolation threshold, we also observe that the conductivity reaches 6.89 S/m at 7 wt% of SWNT loading, which is 14 orders of magnitude higher than that ($10^{-14}$ S/m) of pure polystyrene, and 5 orders of magnitude higher than that ($1.34 \times 10^{-5}$ S/m) of SWNTs (8.5 wt %)/polystyrene composite that was prepared by in situ polymerization.25

Figure 4a shows the measured volume conductivity of PPE-SWNTs/Polycarbonate composites as a function of the SWNT loading. The conductivity of pure polycarbonate is about $10^{-13}$ S/m. We find that the conductivity of PPE-SWNTs/polycarbonate is generally higher that that of PPE-SWNTs/polystyrene at the same SWNT loading. As shown in Figure 4b, we also observe very low percolation threshold at 0.11 wt% of SWNT loading.

The resulting polymer composites also show significant enhancement in mechanical strength. The mechanical measurement showed that 2 wt % of soluble SWNT filling resulted in a 79% increase in the tensile strength of polycarbonate.22 We also observed a stress-induced SWNT alignment in polycarbonate at room temperature, which is impossible to achieve with insoluble SWNTs. The SEM study of the fracture surface indicates excellent interfacial interaction/load transfer between SWNTs and polycarbonate, possibly due to the considerably increased roughness of carbon nanotube surfaces by PPE non-covalent functionalization.

![Figure 2.](image-url)
Figure 3. (a) Room temperature electrical conductivity of PPE-SWNTs/polystyrene composite versus the SWNT weight loading. Dashed lines represent approximate conductivity lower bound required for several electrical applications. (b) Room temperature conductivity of PPE-SWNTs/polystyrene composite as a function of reduced mass fraction of SWNTs.$^{26}$

Figure 4. (a) Room temperature electrical conductivity of PPE-SWNTs/polycarbonate composite versus the SWNT weight loading. Dashed lines represent approximate conductivity lower bound required for several electrical applications. (b) Room temperature conductivity of PPE-SWNTs/polycarbonate composite as a function of reduced mass fraction of SWNTs.$^{26}$

REFERENCES

(22) Chen, J. et al. unpublished results.