

# Calculation of Thermodynamic Stabilities of Polymer/Carbon Nanotube Composites<sup>&</sup>

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## Introduction

It has been demonstrated that the addition of small quantities of carbon nanotubes (CNTs) can dramatically improve thermal and mechanical properties of polymers [1-6]. In many cases, however, this enhancement of properties is limited by the degree to which the CNTs can be uniformly dispersed within the polymer matrix. This appears to be particularly true for flame retarding applications. In a recent work [7], Kashiwagi and co-workers demonstrated that the heat release rates from burning well-dispersed nanocomposites, consisting of single-walled CNTs (SWCNTs) in poly(methyl methacrylate), were significantly lower than those from poorly dispersed samples. Unfortunately, CNTs do not spontaneously mix with most polymers. Instead, they tend to form aggregates consisting of tens or even hundreds of discrete tubes that can become entangled in long rope-like structures [6].

In recent years, some progress has been made in obtaining well-dispersed polymer/nanotube composites using a variety of approaches. These include the addition of surfactants and compatibilizers [8], polymer wrapping [9], and functionalizing the ends and sidewalls of the tubes [10,11]. The widespread implementation of these methods, however, is limited by the absence of a quantitative understanding of the thermodynamics associated with the breakup of the nanotube bundles and the accommodation of the discrete tubes within the polymer matrix.

In this paper, we provide a brief description of a methodology based on molecular mechanics that can be used to estimate the free energy of mixing nanotubes with polymers and apply it to predicting the thermodynamic stability of polystyrene/CNT composites. We anticipate that this approach can be adapted to other systems of interest by tailoring the constituent molecular models to represent the polymers, surfactants, and functional groups under consideration.

## Method

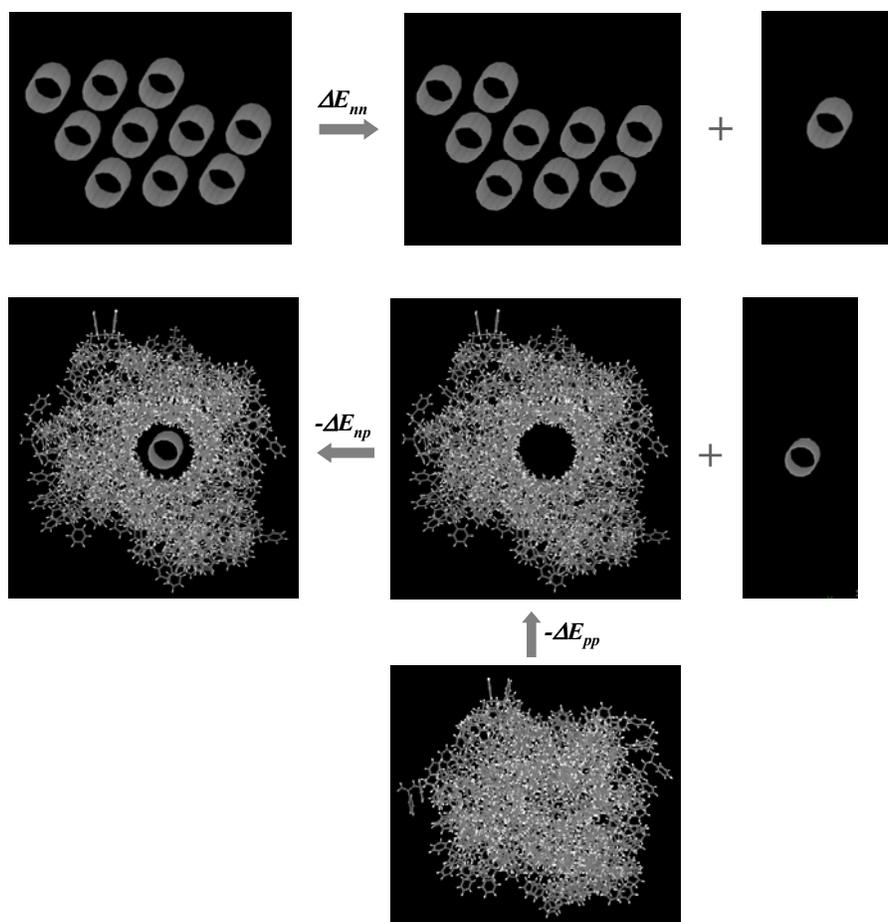
The increase in entropy that accompanies the formation of a mixture is an important factor in determining the miscibilities of small molecules. However, the entropic contribution to the free energy of mixing (normalized per atom or weight of a solute) is expected to be much less significant for large, immobile molecules, such as CNTs and polymers. Moreover, a small increase in entropy associated with the exfoliation of a CNT bundle (the number of spatial configurations attainable by the tubes increases) is compensated by a reduction in entropy due to the restriction of polymer chain motion by the exfoliated tubes. Thus, it should be possible to predict trends in the thermodynamic stability of nanocomposites directly from their enthalpies of

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mixing ( $\Delta H_{mix}$ ). Furthermore, since the nanotubes do not occupy any more volume when they are dispersed in the polymer than they do when they are bunched together, the volume change accompanying the formation of the composite should also be very small implying that  $\Delta H_{mix} \approx \Delta E_{mix}$ .

Unfortunately, an explicit atomistic calculation of the energy of mixing ( $\Delta E_{mix}$ ) is precluded because of the computational demands of evaluating all of the interactions between the atoms in an actual nanocomposite, which might contain nanotubes many microns in length and as many as 1000 carbon atoms in the polymer for every carbon atom in the nanotubes. Instead, the approach we adopted makes use of localized molecular models of the polymer, nanocomposite, and the exfoliated and bundled nanotubes to estimate the relative magnitudes of the energies associated with the polymer-polymer (pp), CNT-CNT (nn) and CNT-polymer (np) interactions. The energy of mixing is then evaluated in terms of a simple path in which the nanotubes are exfoliated from a bundle and dispersed in a distorted polymer with cylindrical cavities to accommodate the nanotubes. From this perspective, the energy of mixing is the difference between the energy required to exfoliate the nanotubes from a bundle and the energy needed to extract the nanotubes from the polymer matrix relative to the relaxed polymer without any nanotubes. The component processes are depicted in Figure 1.



**Figure 1.** Processes involved in the formation of a polystyrene/CNT composite.

Following the logic of this scheme, the energy of mixing can be evaluated from the formulas in Eqs. (1) and (2).

$$\Delta E_{mix} = [\Delta E_{nn}^S - (\Delta E_{np}^S + \Delta E_{pp}^S)] S \quad (1)$$

where,

$$\Delta E_{nn}^S = \frac{\Delta E_{nn}}{S_n}, \Delta E_{np}^S = \frac{\Delta E_{np}}{S_n}, \Delta E_{pp}^S = \frac{\gamma \Delta E_{pp}}{S_n} \quad (2)$$

are calculated from the energy differences of the model processes and  $\gamma$  is a correction factor that is discussed in the next section. In these equations,  $\Delta E_{nn}$  is the energy required to exfoliate a nanotube from a bundle. The magnitude of this term reflects the strength of the interaction between nanotubes. The second term,  $\Delta E_{np}$ , is the energy needed to extract a nanotube from a polymer/CNT agglomerate that represents the environment of the nanocomposite in the vicinity of the nanotube. This term accounts for the interactions between the nanotube and polymer. The last term,  $\Delta E_{pp}$ , is the energy of closing of the cylindrical cavity occupied by the nanotube in the polymer-nanotube agglomerate. This closing results in a decrease in surface area and a corresponding decrease in energy due to the increase in the number of attractive polymer-polymer interactions.

The individual terms in Eq. (2) are normalized by dividing by the surface area of the model nanotube,  $S_n$ , to facilitate the extrapolation of the results obtained from the atomic length scales of the molecular models to the much larger dimensions that prevail in real materials. Thus, as indicated in Eq. (1), the sum of these component energies is multiplied by the total surface area of nanotubes,  $S$ , in calculating the energy of mixing associated with the formation of a real nanocomposite.

## Application

The methodology described in the preceding section was applied in an attempt to understand the factors that determine the thermodynamic stability of polystyrene/CNT composites. Polystyrene (PS) was chosen for the first application because it has aromatic rings, which should interact favorably with the aromatic rings that comprise the nanotubes based on the premise that “like dissolves like.” The molecular models of PS, PS/CNT agglomerates, nanotube bundles, and separated nanotubes were built using a commercial software package (Material Studio<sup>\*</sup>). The PCFF force field [12] was used for optimization of the model structures and energy calculations.

The uncapped (7,0) SWCNTs with radius,  $R = 0.28$  nm, were used in the models. From them, we constructed three nanotube bundles. The largest one, which is depicted in Figure 1,

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<sup>\*</sup> Certain commercial equipment, instruments, materials or companies are identified in this paper in order to adequately specify the experimental procedure. This in no way implies endorsement or recommendation by NIST.

consisted of 10, 3.6 nm long nanotubes arranged in a closest packing structure. Comparable results were obtained from the models consisting of 7, 3.6 nm long nanotubes and 7, 7.3 nm long nanotubes. The polymer/CNT agglomerates were constructed by minimizing the energies of the intermediate structures obtained by adding successive polymer chains. The structure of one of these polymer-nanotube agglomerates is depicted in Figure 1. On this basis, it was determined that 12 chains were sufficient to achieve convergence of the polymer-nanotube interaction energies to the limit of infinite dilution. The lengths of the polymer chains, which were adjusted to ensure that they covered the full surface of the nanotube, were 17 and 34 monomers for agglomerates containing the 3.6 nm and 7.3 nm nanotubes, respectively. The density of the polymer matrix in these polymer/CNT agglomerates was about 1000 kg/m<sup>3</sup>.

The effects of increasing the lengths of the model nanotubes from 3.6 nm to 7.3 nm can be seen in the data presented in Tables 1 and 2. These results seem to justify the intuitive notion that, for a specified diameter, the energies of interaction per unit area are almost independent of the lengths of the nanotubes. Moreover,  $\Delta E_{nn}^S$  appears to be independent of both the length and number of nanotubes in the bundle.

**Table 1.** Models of SWCNT Bundles.

Number of Nanotubes	Length of Nanotube (nm)	Surface Area of Nanotube (nm <sup>2</sup> )	Number of Carbon Atoms/Area (nm <sup>-2</sup> )	$\Delta E_{nn}^S$ (kJ/mol-nm <sup>2</sup> )
7	3.6	6.3	39.8	159
7	7.3	12.9	39.1	163
10	3.6	6.3	39.8	162

**Table 2.** Models of PS/SWCNT Agglomerate.

Length (nm)	$R_{pn}$ (nm)	$R_c$ (nm)	$\gamma$	$\Delta E_{np}^S$ (kJ/mol-nm <sup>2</sup> )	$\Delta E_{pp}^S$ (kJ/mol-nm <sup>2</sup> )
3.6	1.75	0.525	0.87	176	-95
7.3	1.90	0.525	0.88	160	-99

The dependence of these energies on the radius of the constituent nanotubes, however, is more complicated. Consider first the  $\Delta E_{nn}^S$  term. If the number of atoms per unit surface area is independent of the radius of the nanotube (which is tantamount to assuming that the aromatic rings have the same structures), then it can be shown that the energy of extraction of a CNT from a bundle (per unit surface area of the nanotube) will decrease approximately in accordance with Eq. (3) [13].

$$\Delta E_{nn}^S = \frac{k'_{nn} l \sqrt{R}}{2\pi R l} = \frac{k_{nn}}{\sqrt{R}} \quad (3)$$

Here  $R$  is the radius and  $l$  is the length of the component nanotubes. The decrease in  $\Delta E_{nn}^S$  arises from the simple fact that the average distance between two parallel cylindrical surfaces (with the

same radius) increases from their distance of closest approach with increasing radius. Since the atoms that comprise each of the two interacting nanotubes are on average farther apart in large diameter nanotubes (assuming that their distance of closet approach remains the same), the attraction between them diminishes thereby reducing the cohesive energy per unit surface area of the bundle.

A similar analysis can be applied to both  $\Delta E_{np}^S$  and  $\Delta E_{pp}^S$ . The later of these two terms is proportional to the surface energy of the polymer, which increases linearly with the number of atoms that are brought from the interior to the surface. The area of the nanotube cavity in the polymer matrix is  $2\pi(R+d)l$ , where  $d = 0.25$  nm is the average distance between the polymer and the surface of the nanotube. Of course, the outer surface of the polymer must also expand to accommodate the nanotube. The correction factor,

$$\gamma = \frac{R_c}{R_c + R_{pn} - \sqrt{R_{pn}^2 - R_c^2}}, \quad (4)$$

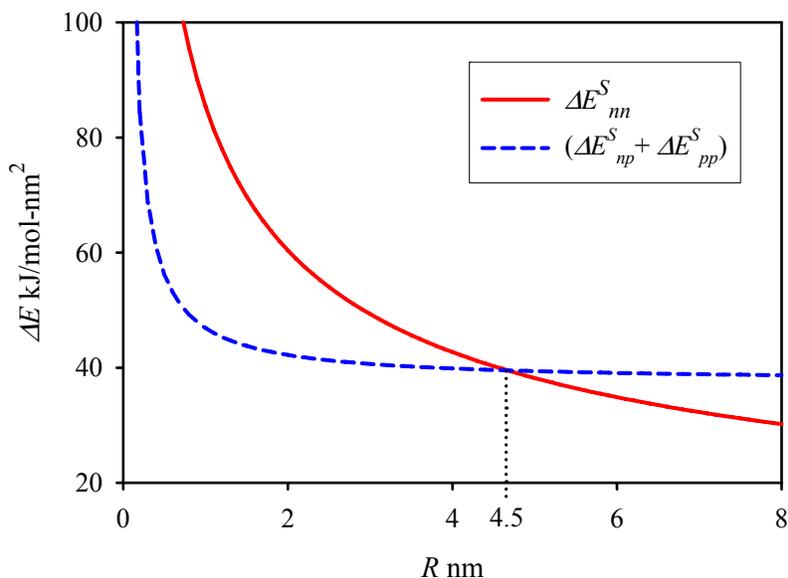
represents the fraction of the total increase in surface area due to the formation of the cylindrical cavity. In Eq. (4),  $R_c = R+d$  is the radius of the cylindrical cavity and  $R_{pn}$  is the radius of the polymer-nanotube agglomerate, which is also assumed to be cylindrical in shape. This correction is needed to extrapolate the results from the model calculations, where the change in the outer surface of the cylinder representing the polymer-nanotube agglomerate is significant, to realistic dimensions, where this contribution is negligible. The values of this correction factor for the PS/SWCNT agglomerates are listed in Table 2.

Consider next the  $\Delta E_{np}^S$  term. From Figure 1, it appears that the polymer effectively encircles the nanotube. The distance between the surface of the nanotube and the polymer ( $d$ ) is determined by the van der Waals radii of the interacting atoms and should be relatively independent of the diameter of the nanotube. Therefore, the nature of polymer-nanotube interaction is similar to the case of two parallel sheets, for which the energy of interaction per unit surface area is constant. This is, in fact, the limiting behavior of  $\Delta E_{np}^S$  as  $R \rightarrow \infty$ . However, because of their concentric arrangement, the number of interactions between atoms on the cylindrical surface of the polymer and atoms on the surface of the nanotube (per unit area of the nanotube) increases as the ratio of the surface areas. Thus, we infer that both  $\Delta E_{np}^S$  and  $\Delta E_{pp}^S$  scale the same way with nanotube radius so that

$$\Delta E_{np}^S + \Delta E_{pp}^S = \frac{k'_{np+pp} 2\pi(R+d)l}{2\pi Rl} = k_{np+pp} \left(1 + \frac{d}{R}\right). \quad (5)$$

The averages of the values of  $\Delta E_{nn}^S$  and  $(\Delta E_{np}^S + \Delta E_{pp}^S)$  reported in Tables 1 and 2 were extrapolated as a function of nanotube radius using Eqs. (3) and (5). The results of these extrapolations are plotted in Figure 2. At  $R = 4.5$  nm, the energy needed to exfoliate the nanotubes falls to the point where it is offset by the energy released as a result of submerging the nanotubes into the polymer and thermodynamic neutrality of the mixing is attained. Thus, we

predict that it should be possible to obtain stable, exfoliated nanocomposites by blending CNTs having diameters greater than about 9 nm with polystyrene. Since SWCNTs are typically much smaller than this (1.0–1.4 nm in diameter [14]), we conclude that thermodynamic neutrality is never attained when SWCNTs are added to PS. On the other hand, our results do indicate that it should be possible to make thermodynamically stable PS/CNT composites from multi-walled carbon nanotubes, which have diameters ranging from about 10 to almost a 100 nm [15].



**Figure 2.** Contributions to the energy of mixing as functions of nanotube radius.

## Conclusion

The approach outlined in this paper should be applicable to other polymer/nanotube systems provided that the molecular models used in the calculations are modified to reflect their chemical natures. It should be kept in mind, however, that thermodynamics may actually be less important than kinetics in determining whether a nanocomposite will be stable. For this reason, this approach may not offer a definitive answer to the question of whether or not it is possible to obtain a well-dispersed nanocomposite from a given set of components. Nevertheless, it does provide a quantitative basis for assessment of relative stability of various compositions. We hope to be able to demonstrate this in the future, by using this approach to examine effects of the nature and degree of functionalization of SWCNTs on the thermodynamic stability of nanocomposites.

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