



*Dedicated to Prof. Bogdan C. Simionescu
on the occasion of his 75th anniversary*

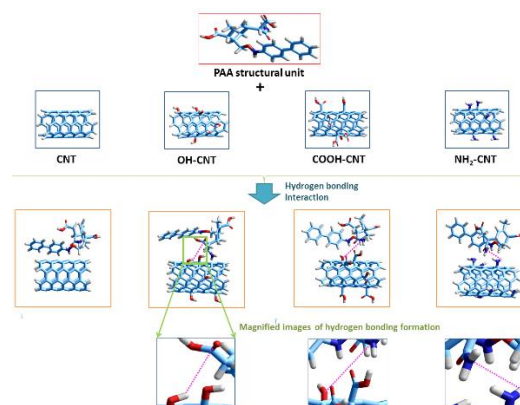
POLYIMIDE PRECURSOR/FUNCTIONALIZED CARBON NANOTUBES: MOLECULAR MODELING AND PHYSICAL PROPERTIES THEORETICAL EVALUATION

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This article explains the influence of –OH, –COOH, and –NH₂ functional groups, bounded to carbon nanotubes, on the interactions occurring in composites having as matrix a polyimide precursor. The molecular modeling is used to visually reveal the optimized conformation of the polyimide precursor structural unit, carbon nanotubes with or without functional groups and corresponding composites where hydrogen bonding interactions is formed. Also, based on molecular modeling, quantitative structure activity relationship parameters and binding energies are calculated, indicating that the interaction energy between the matrix and the filler is greater as the functional group polarizability is higher. The theoretically estimated electrical conductivity of the composites increases by the addition of the filler and it is the highest for the ones containing carbon nanotubes functionalized with –OH. The theoretical analysis of the thermal conductivity of the composites reveals a better heat conduction for the same mentioned filler, being increased during the temperature rise. This kind of study is necessary to predict certain properties of the composites before synthesis, thus avoiding the wasting of raw compounds.



INTRODUCTION

Over the past decades, polymer-based materials introduced many advantages in electronic applications, such as relatively diminished production costs, lightweight, relatively facile processability and exceptional flexibility. Such multiphase systems have found practical utility in this industrial area for a variety of device components, such as electrodes,¹ foldable supports for integrated circuits,² anti-reflective

layers,³ amplifiers,⁴ and capacitors.⁵ For additional improvement of the overall performance, the physico-chemical properties of polymers can be adapted by inserting fillers having advanced properties. Among the most investigated additive nanoparticles, carbon nanotubes (CNTs) have proved to display an extremely good balance of electrical, mechanical, and thermal characteristics.⁶ Hence, their incorporation into

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polymers is highly beneficial even at low amounts.^{7,8} Moreover, the composite properties are impacted by the level of compatibility between the CNT and the polymer.⁹ This might be accomplished by chemical modification of the CNT nano-filler to link specific functional groups, which can better interact with the surrounding macromolecules.^{10,11} By following such procedure, the dispersion properties and interface interactions can be meliorated.¹² The pre-treatment of the CNT reinforcement agent is very useful for creating supplementary conductive paths inside the composite medium. In this regard, Maity *et al.*¹³ showed that by varying the degrees of CNT functionalization, it is possible to control the electrical conductivity of the corresponding polymer composite. Many reports¹⁴⁻¹⁸ deal with unraveling of the relation among the final composite electrical properties and some particular factors, like the type of bonding interactions occurring between the CNT and the functional moiety and the density of the functional groups and the CNT geometry. Another factor, which is not fully detailed in literature, is represented by the sort of the functional groups onto the CNTs and their role in augmenting the electrical conduction features of the polymer composites.

Many categories of polymers are currently employed as matrices for the fabrication of the CNT-based composites, such as polystyrene,¹⁹ poly(methyl methacrylate),²⁰ polyvinyl alcohol,²¹ polyurethane,²² polysulfone,²³ polysiloxane²⁴ and polyimide.²⁵ In the latter case, reinforcement of polyimides with CNTs would result in thermally resistant products with great electrical and mechanical properties.²⁶ However, for advanced compatibility, the polymer must contain functional groups, which enable the enhancement of the interactions with the CNTs and therefore producing a lower electrical or thermal resistance at the polymer/filler interface.²⁷ According to our knowledge, the polyimide precursors (*i.e.* poly(amic acid)s – PAA) are not extensively studied in the literature,²⁸⁻³⁰ but they contain two kinds of functional groups (–CONH and –COOH), which are beneficial for interacting with functionalized CNTs. As far as we know, there are no reports on composites derived from PAA filled with CNTs.

The main idea of this work is to elucidate the influence of various functional groups attached on CNTs on the interactions occurring in composite having a PAA as matrix. Molecular modeling enabled visualization conformation of both filler (in the presence/absence of functional groups) and PAA structural unit. Based on the achieved computation data, the calculation of the quantitative structure

activity relationship (QSAR) and interaction energy was performed. Furthermore, a theoretical analysis of the electrical and thermal conductivity of the composites based on PAA and various percent of CNT fillers was made. The outcome of this sort of investigation is useful for prediction of a composite properties allowing to extracted new insights essential for optimal design of a material prior to its synthesis, without wasting raw compounds in an inefficient synthesis.

RESULTS AND DISCUSSION

Molecular modeling

A relatively new trend in the design of polymer-based materials relies on computer simulations, which helps to visualize the targeted chemical structures in precise conditions. Such procedure greatly lowers the cost of product optimization during the polymerization or composite synthesis. Moreover, it can effectively forecast the optimal conformational features of the matrix in the presence of an additive. In this work, a polyimide precursor (PAA) was chosen as matrix for filling with CNT (with or without the functional groups). The PAA was designed from a flexible and aliphatic dianhydride (3a,4,5,7a-Tetrahydro-7-methyl-5-(tetrahydro-2,5-dioxofuran-3-yl)isobenzofuran-1,3-dione) and a rigid and aromatic diamine (4,4'-Diaminobiphenyl). The optimized geometry of the structural unit of this PAA is depicted in Fig. 1. Also, the CNT was modeled before and after functionalization with –OH, –COOH, and –NH₂ (see Fig. 1). For the simulations of these fillers, the following structural features were imposed: the chiral vector was described by $m = 4$ and $n = 4$, while the tube length was chosen to be $l = 1$ nm. The conformational aspects of these carbon-based fillers during interaction with the structural unit of the polyimide precursor were computed, as seen in Fig. 1. All the computed data from Fig. 1 are attained for lowest energy conditions. It is remarked that the functionalized filler interacts with the –COOH or –CONH groups from the PAA matrix via hydrogen bonding interactions.

The simulations also facilitated the estimation the following QSAR characteristics: van der Waals-surface-bounded molecular volume (V_w), partition coefficient ($\log P$) and polarizability (α). The obtained values for the individual PAA and (pristine/modified) CNT, but also for the corresponding systems are listed in Table 1. The $\log P$ is linked to the hydrophilic

or hydrophobic feature of a substance. Since the evaluated $\log P$ data have positive values for individual components and composite systems, it seems that the samples present hydrophobic character. The polarizability values tend to be smaller for the PAA in comparison to the CNT having/lacking

functional groups. Also, it appears that the type of the functional groups linked to the CNT is impacting the polarizability, which varies in the next order: CNT-COOH > CNT-NH₂ > CNT-OH > CNT. This result is reflected in the polarizability of the PAA/CNT composites.

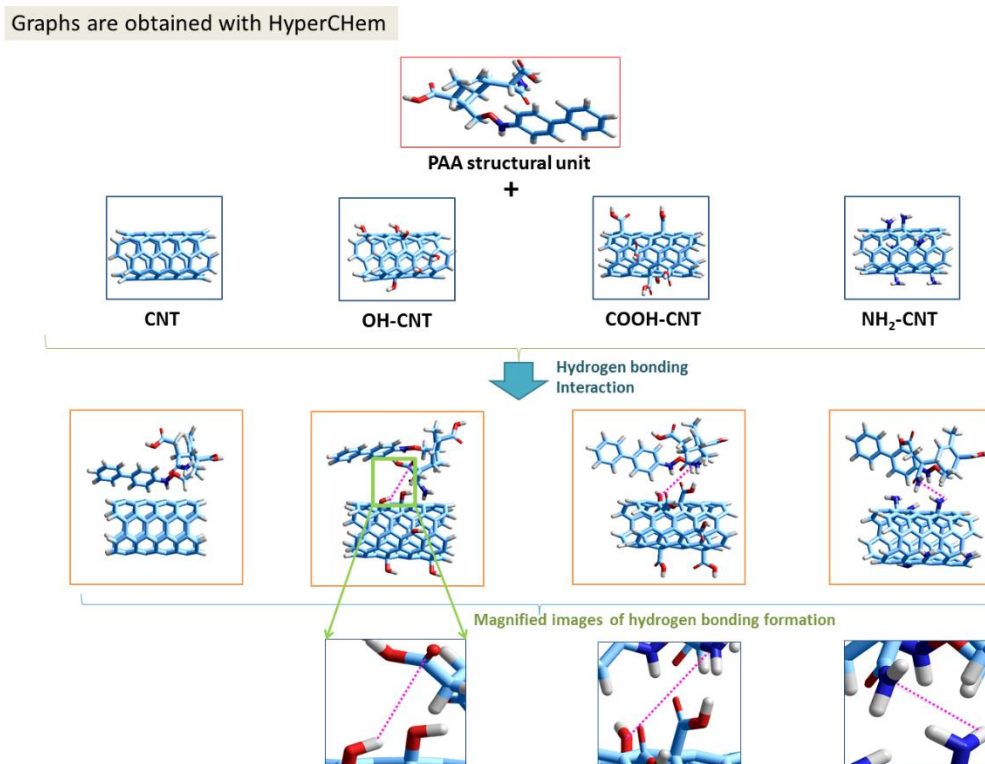


Fig. 1 – Images resulted from the molecular modeling of optimized PAA structural unit, CNT filler having/lacking functional groups and PAA/CNT systems where hydrogen bonding interactions occur.

Table 1

QSAR parameters extracted from the performed computations for PAA, pristine/functionalized CNT and PAA/CNT systems

Sample/system	V_w [\AA^3]	$\log P$	α [\AA^3]
PAA	412.69	2.95	47.85
CNT	695.18	14.42	134.00
CNT-OH	748.52	9.10	135.13
CNT-NH ₂	774.48	8.19	139.42
CNT-COOH	856.02	11.92	146.66
PAA/CNT	1112.98	13.87	181.85
PAA/CNT-OH	1161.95	13.88	182.99
PAA/CNT-NH ₂	1187.17	15.48	187.27
PAA/CNT-COOH	1265.32	9.13	194.51

According to Mulliken charges and basic chemical characteristics, the probable configurations of PAA/CNT systems were computed and optimized using molecular mechanics force field. The Parametric Method 3 (PM3) setting was used to achieve the calculation of the interaction energy between PVA and CNTs, within Restricted Hartree Fock (RHF) formalism.³¹ The interaction energy (ΔE) assessment was accomplished on basis of the equation (1):³²

$$\Delta E = E_{\text{PAA/CNT}} - (E_{\text{PAA}} + E_{\text{CNT}}) \quad (1)$$

where ΔE is the PAA/CNT interaction energy, whereas E_{PAA} is the binding energy of the matrix and E_{CNT} is the binding energy of the pristine or modified filler.

For any molecular system, the bigger values of ΔE are reflecting a larger binding energy and, as a result, the conformations with greatest stability. It can be seen in Fig. 2a that regardless the presence of

functionalities on CNTs, they have higher binding energy in regard to the polyimide precursor. For the composites, it is noticed that as the polarity of the

functional groups from CNT is larger, the interaction energy is increasing, denoting greater stability of the system.

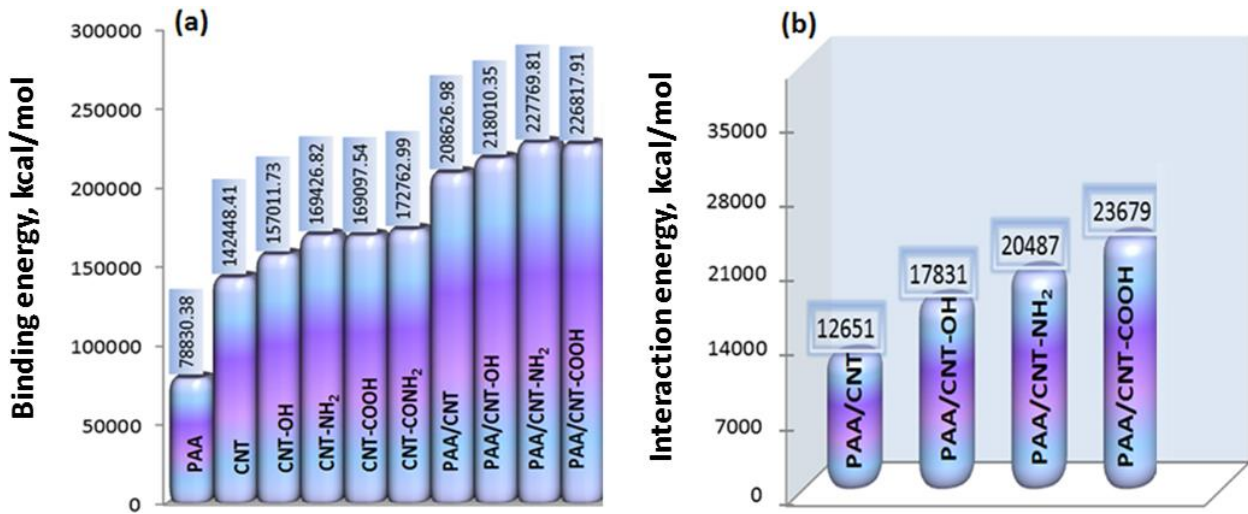


Fig. 2 – Bar charts representing the variation of: a) binding energy of individual PAA and (pristine/modified) CNT components; b) interaction energy for each PAA/CNT system.

Evaluation of the electrical conductivity

The electrical conduction properties of a composite material can be described by mixing rules, such as parallel model, shown in equation (2):

$$\sigma_c = \sigma_p w_p + \sigma_f w_f \quad (2)$$

where σ is the symbol of the electrical conductivity and w is for the weight fraction, while index “c” denotes the composite, “p” denotes the polymer, “f” denotes the CNT filler.

To determine the composite electrical features, it is essential to obtain the values of the individual components. For a polymer matrix, the electrical resistivity (reverse of conductivity) of the PAA was estimated based on connectivity index procedure proposed by Bicerano,³³ as indicated by equation (3):

$$\log R = 23 - 2 \cdot \varepsilon \quad (3)$$

where R is the electrical resistivity and ε is the dielectric constant of the material.

In the case of polymers, the dielectric constant can be easily estimated by means of Lorentz-Lorenz relation:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{R_m}{V} \quad (4)$$

where R_m depicts the molar refraction, and V indicates the molar volume.

The molar refraction and molar volume are deduced via group contribution of each sub-structure.³⁴ For the studied PAA structure, a molar refraction of 101.115 cm³/mol and a molar volume of 241.655 cm³ were obtained. These data lead to a dielectric constant of 3.158 was achieved and hence a resistivity of $4.831 \cdot 10^{16} \Omega \text{ cm}$. The conductivity of pristine and functionalized filler was previously reported, indicating great conduction abilities.³⁵ These data and that of the PAA were inserted in the above relation and the composite electrical performance is illustrated in the Fig. 3. The parallel model reveals that the composite conductivity is increased by the amount of the CNT in wt%. Upon the functionalization with -NH₂ the lowest values are attained, while for CNT-OH the conductivity is still high.

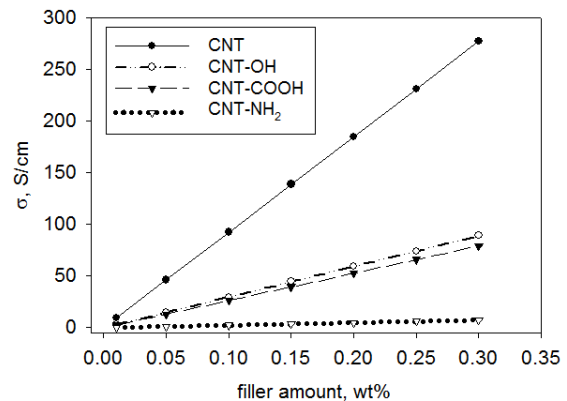


Fig. 3 – The variation of the electrical conductivity of the PAA filler with pristine/modified CNTs with the reinforcement degree.

Evaluation of the thermal conductivity

Heat transfer via conduction is taking place by collision of atoms inside the medium. The level of heat transfer is affected by the temperature gradient and the thermal conduction of the considered environment (e.g. polymer composite). When the temperature has a known constant value, the relation between the electrical and thermal conductivities can be quantified by Wiedemann-Franz law,³⁶ seen in equation (5):

$$\kappa/\sigma = LT \quad (5)$$

where κ is the thermal conductivity, L is a proportionality constant and T is the temperature.

The Wiedemann-Franz expression was applied to the designed PAA/CNT systems by employing the conductivity values determined by parallel model at highest reinforcement level. The obtained thermal conductivity values of all the samples are illustrated in the Fig. 4. The data reveal that, when the temperature is enhanced, the thermal conduction ability of the samples at 30 wt% filler is increasing. Also, the type of the functional group is affecting the magnitude of κ parameter. The lowest heat conduction is observed for composite with the filler CNT-NH₂, while the best are remarked for the sample with pristine CNT, followed by that containing CNT with hydroxyl functionality.

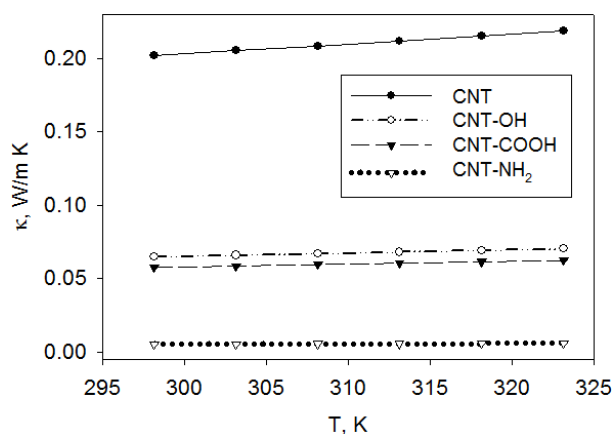


Fig. 4 – Thermal conductivity against temperature for PAA filled with pristine/modifier CNTs at 30 wt% filler.

EXPERIMENTAL

Molecular modeling was done by HyperChem (demo version) to visualize the conformation of the PAA and pristine/modifier CNTs at minimized conditions. The molecular QSAR parameters were extracted from the computations. Semi-empirical

mechanic PM3 calculation within Restricted Hartree Fock (RHF) formalism was utilized to estimate the interaction energy.

CONCLUSIONS

The properties of the PAA composite are affected by the type of the functional groups attached onto the surface of the CNT filler. The interaction energy PAA-filler appears to be greater as the functional group polarizability is higher. The electrical conductivity of the samples is increased by the addition of carbon-based filler and is highest for the composite with CNT-OH. At 30 wt % loading, the heat conduction is better for the sample with the same filler and it is augmented upon temperature enhancement. Such materials present applicative potential in electronics as flexible electrodes or heat sinks.

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