

# Synthesis, morphology investigation and thermal mechanical properties of dopamine-functionalized multi-walled carbon nanotube/poly(amide-imide) composites



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## ABSTRACT

Here, poly(amide-imide) (PAI) composites containing multi-walled carbon nanotubes (MWCNT) were synthesized with solution casting method. To improve the dispersion and compatibility with the polymer matrix the MWCNT was surface-modified with dopamine biomolecule under microwave irradiation. The prepared dopamine-functionalized MWCNT (MWCNT-Dop) was characterized for their structure, morphology, and thermal behavior employing Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis, field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). The results consistently confirmed the formation of dopamine functionalities on MWCNT. The MWCNT-Dop/PAI hybrid films were also characterized extensively using FT-IR and XRD techniques. The microstructure of the composites was studied by FE-SEM and TEM, in terms of the dispersion state of the nanotubes and the polymer-nanotube interface. The thermal behavior and mechanical properties of the resultant composites were also studied. In comparison with neat PAI, the MWCNT-Dop reinforced composites possess higher thermal stability, tensile strength and Young's modulus.

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## 1. Introduction

Carbon nanotubes (CNT) have received considerable attention as a new class of nanomaterials. Regardless of being single-walled CNT (SWCNT) or multi-walled CNT (MWCNT), CNT presents several interesting properties such as high aspect-ratio, ultra-light weight, tremendous strength, high thermal conductivity and remarkable electronic properties ranging from metallic to semiconducting [1]. The chemical bonding of CNT is composed entirely of  $sp^2$  carbon-carbon bonds. This bonding structure—stronger than the  $sp^3$  bonds found in diamond—provides CNT with extremely high mechanical properties [2]. Owing to their exceptional elastic modulus and strength, the utility of using CNT as reinforcements in organic polymers began when CNT was discovered by Iijima in 1991 [3]. Compared with traditional reinforcing agents such as glass fibers, CNT is much more efficient in improving the composite properties because of their extremely high aspect ratio. However, achieving a high degree of dispersion of CNT in a polymer

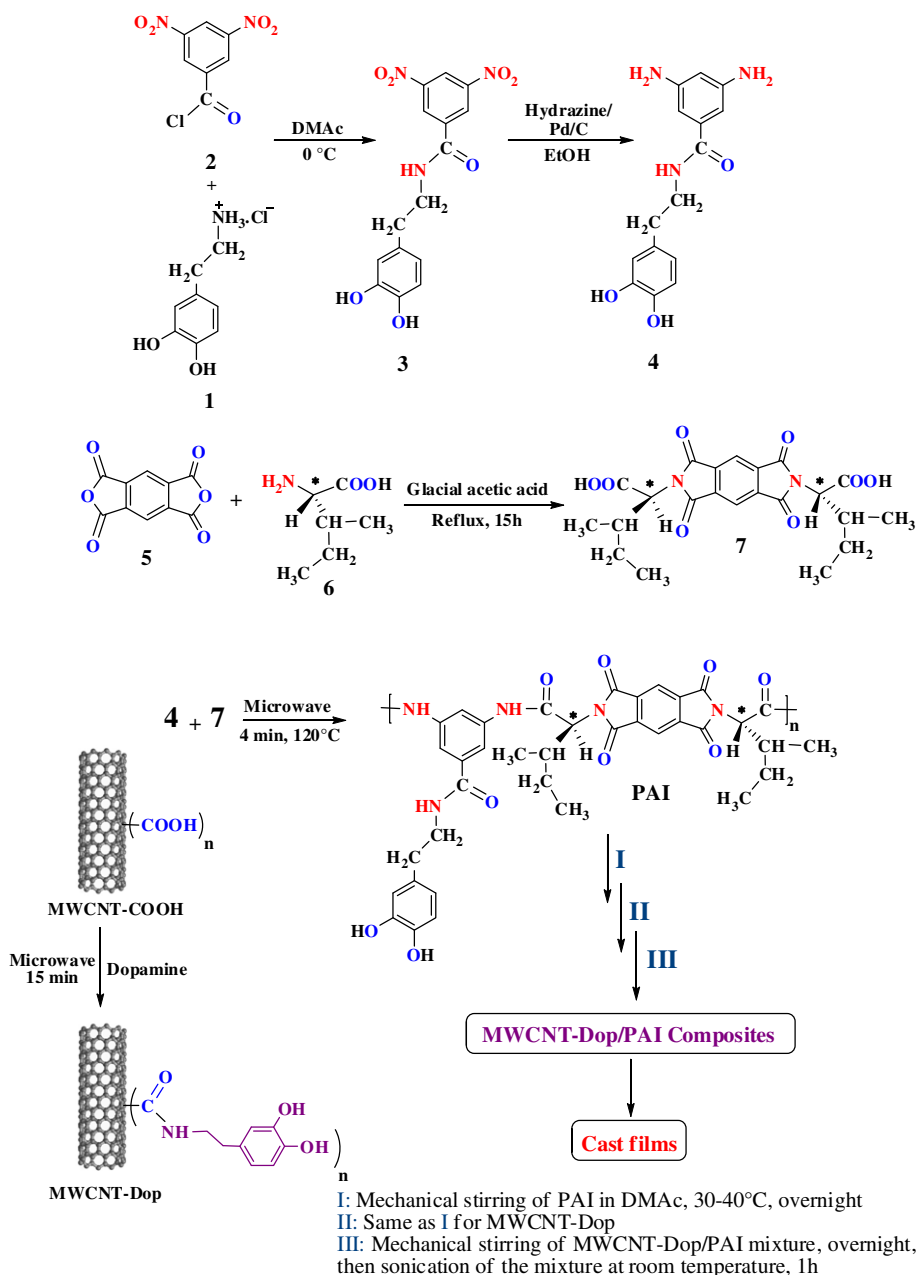
matrix is challenging due to agglomeration and aggregation into bundles [4–6]. To address these problems, several strategies for synthesis of the nanotube-reinforced polymer-matrix composites have been developed, including solution casting with ultrasonication [7–9], melt-mixing [10,11], surfactant-assisted processing [12], surface modification strategies (e.g. grafting and polymer wrapping) [13], and in situ polymerization of monomers in the presence of CNT [14–16]. Local strain in CNT, which arises from pyramidalization and misalignment of the  $\pi$ -orbitals of the  $sp^2$ -hybridized carbon atoms, makes nanotubes more reactive than a flat graphene sheet, thereby paving the way to covalently attach chemical species to nanotubes. This covalent functionalization of nanotubes can improve nanotube dispersion in solvents and polymers [4]. Covalent functionalization can also provide a means for engineering the nanotube/polymer interface for optimal composite properties. With respect to mechanical properties, for example, the interfacial adhesion could be modified through covalent or non-covalent interactions between the functional group on the nanotube and the polymer matrix to maximize load transfer [17–19]. Many approaches have been tried so far to carry out chemical functionalization of carbon nanotubes. For example, the generation of surface hydrophilic substituents such as carboxylic, hydroxyl or sulfonic acid groups by suitable chemical method is rather easy for their wide use in medical and biological applications [20–22]; since, these functional groups

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provide necessary sites for covalent or non-covalent coupling of CNT. In addition to the improvement of the performance of CNT, the development of new functionalization methods is of immense importance, since through proper functionalization it is possible to impart improved or altogether new properties like non-toxicity or biocompatibility, which could be essential for biological applications. Many of the functionalization reactions are required to be carried out over long period of time. For example, for carboxylation or hydroxylation, the reaction mixture is typically refluxed in concentrated  $\text{HNO}_3$  or acid mixture for >10 h, which is a tedious and time consuming process [23]. In recent years, the microwave irradiation is suggested as a simple, inexpensive and rapid approach for functionalization of CNT. It has also shown to result in lower structural defects on CNT surface compared with the conventional methods. A considerably higher value of the solubility of CNT has been observed in aqueous media within a period of a few minutes by this approach [24,25].

Design and synthesis of copolymers with the introduction of flexible linkages, such as amide, ester, ether, and sulfide linkages between the aromatic rings of the main chain, is a successful way to create polymers more tractable. Poly(amide-imide)s (PAI)s, that have amide and imide linkages in the main backbone, are a class of high performance materials which possess desirable characteristics with the merits of both polyamides and polyimides, for example, exceptional thermomechanical properties at high temperature with good dimensional stability, excellent creep, and chemical resistance and so they have found extensive use in many engineering applications such as molded parts for the space shuttle, engine parts of world-class racing cars, and many other critical components like membranes for ultrafiltration [26,27]. In the recent last decades, the effect of adding CNT on the properties of PAIs has been investigated by many researchers. Some of possible promising applications of these composites are including gas storage, electrochemistry, biosensing application, photovoltaics and photoelectrochemical



Scheme 1. Preparation process of diacid 7, diamine 4, PAI, and MWCNT-dop/PAI composites.

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