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Full Length Article

Surface modification of carbon nanotubes using 3-aminopropyltriethoxysilane to improve mechanical properties of nanocomposite based polymer matrix: Experimental and Density functional theory study

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ABSTRACT

In current study we combined theoretical and experimental studies to evaluate the effect of functionalization and silanization on mechanical behavior of polymer-based/CNT nanocomposites. Epoxy was selected as thermoset polymer, polypropylene and poly vinyl chloride were selected as thermoplastic polymers. The whole procedure is divided to two sections . At first we applied density functional theory (DFT) to analyze the effect of functionalization on equilibrium distance and adsorption energy of unmodified, functionalized by —OH group and silanized epoxy/CNT, PP/CNT and PVC/CNT nanocomposites and the results showed that functionalization increased adsorption energy and reduced the equilibrium distance in all studied nanocomposites and silanization had higher effect comparing to OH functionalizing. Then we prepared experimental samples of all mentioned nanocomposites and tested their tensile and flexural strength properties. The obtained results showed that functionalization increased the studied mechanical properties in all evaluated nanocomposites. Finally we compared the results of experimental and theoretical sections with each other and estimated a suitable agreement between these parts.

1. Introduction

The use of reinforcements for improving thermal, mechanical and electrical properties of polymer based nanocomposites is seen to be widely extended in early engineering applications. The properties of such nanocomposites depend on interfacial adhesion between reinforcing item and polymer matrix. Among different applicable reinforcements such as: carbon fiber, glass fiber, nano Silica, nano clay, etc, Carbon nanotubes (CNTs) are highly applied in this case due to their superior physical and mechanical features, good stiffness, high thermal and electrical conductivity and excellent strength [1,2]. Therefore many studies have focused on incorporating CNTs to different polymer matrixes to enhance mechanical properties of CNT/polymer nanocomposites [3–5]. Yokozeki et.al, studied the mechanical properties of carbon/epoxy nanocomposite reinforced with cup-stacked carbon nanotubes (CSCNT) and reported that the stiffness and strength of obtained nanocomposite were better than non- reinforced carbon/epoxy nanocomposite [6]. Gojny and his coworkers used standard calendaring technique to produce DWCNT/epoxy nanocomposite with low nanotube content, their results showed good dispersion of double walled CNT in epoxy matrix. Also fracture toughness, Young's Modulus and strain to failure of evaluated nanocomposites were significantly higher than those of neat epoxy [7].

There is an obvious relationship between properties of CNT/Polymer nanocomposites and morphology of CNT-reinforced/polymer. The main found problem in this matter is weak interaction between CNT and matrix. Furthermore non-homogeneous dispersion of CNTs in polymer matrix leads to agglomeration of CNTs in polymer which weakens expected properties [8]. A considerable number of studies have been done in order to find an effective method to disperse CNT in polymer matrixes uniformly and increase interfacial adhesion of mentioned nanocomposite [9–11]. One of these techniques is surface modification of nanoparticles especially CNTs by chemical methods named chemical functionalization, which can be used for reducing CNTs dispersibility in polymer matrix and improving the

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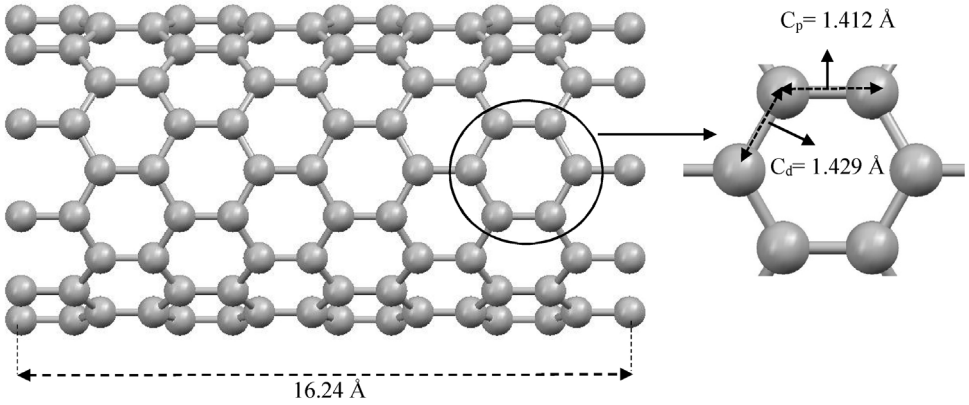

Fig. 1. Optimized structure and geometrical structure of unmodified CNT.

interfacial adhesion and also adsorption energy of CNT/polymer nanocomposite.

Functionalizing CNTs with different agents like: hydroxyl group and silane-modification simplifies uniform dispersion of CNTs in polymer matrix and also enhances its physical and chemical characteristics for being used in specific demands [12–16]. A vast number of experimental and theoretical researches have been done with this purpose. Shi-Zhao kang and his group modified multi walled CNT with hydroxyl group and found that carbon nanotube modified with hydroxyl group could be highly dispersed in ethanol and created a stable solution, moreover morphology and diameter of MWCNT were well preserved under modification [12]. Ji Hoon Lee et al. compared thermal and mechanical properties of unmodified, acid-modified and silane-modified MWCNT and reported that elastic modulus of silane-modified CNT was18% and 13% higher than elastic modulus of unmodified and acid-modified CNT respectively. Also tensile strength of silane- modified CNT showed similar behavior comparing to others [14]. J.H lee and his colleagues evaluated the effect of acid and silane-modification on tensile and thermal properties of CNT/Basalt/epoxy nanocomposite and reported that Young's modulus and tensile strength of silane/CNT/Basalt/epoxy nanocomposite were considerably higher than those of unmodified nanocomposite [15]. Johan Kathi functionalized MWCNT with a mixture of sulfuric acid and nitric acid (f-MWCNT) and then silanized the modified MWCNT with 3- aminopropyltriethoxysilane (3-APTS) and obtained that silanization improved chemical adaptability of MWCNT. Moreover they observed surface morphology after silanization using FE-SEM and showed a clear distribution of MWCN. Also morphology remained unchanged after functionalization [16].

In addition, computational atomistic modeling methods which are based on molecular dynamics (MD), semi empirical methods and AB initio calculations can be employed in order to simulate adsorption energy, mechanical and electrical properties of f-MWCNT/polymer nanocomposite [17–19]. Density functional theory (DFT) which is a subset of *ab-initio* methods is a renowned atomistic modeling method and has high potential for being used in chemistry, physics and science of materials [20–25]. This method calculates for more details about the electrons and the ions and can provide more interactions and correlations, such as electron–electron, electron–ion and ion–ion interactions comparing to other simulation techniques [26]. Pan et al. applied DFT calculations to investigate the effect of functionalizing single wall CNTs with OH group on electronic and optical properties of the modified SWCNT and confirmed ban-gap reduction and improvement in optical and electrical properties [27].

In current study we used DFT calculations to investigate the effect of functionalization and silanization of SWCNT (single-walled carbon nanotube) on adsorption energy between mentioned nanomaterial and polymer matrix. To find the relationship between adsorption energy and mechanical properties, PVC and PP were selected as Thermoplastic polymers and epoxy was employed as thermoset polymer to fabricate nanocomposite samples and three groups of nanocomposites including: SWCNT/polymer, SWCNT-OH/Polymer and Silanized SWCNT/polymer were prepared. Tensile and flexural tests were done on them to consider mechanical properties of mentioned nanocomposites. At last, the mechanical results obtained from experimental section and adsorption energy yield from computational calculation were compared with each other.

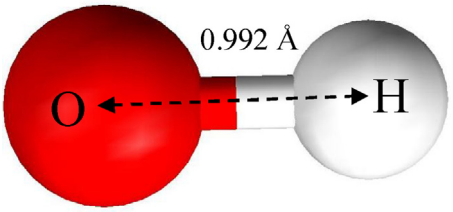

Fig. 2. The optimized structure of an individual hydroxyl group (—OH) molecule.

2. Experimental

2.1. Details of materials

SWCNT used in current study (with purity more than 90%, with an outer diameter 1–2 nm and length about 5–30 μm) and SWCNT-OH (with purity more than 90%, —OH content of about 3.96 wt%, with an outer diameter 1–2 nm and length of about 5–30 μm) were purchased from Research Institute of Petroleum (RIPI). Silane functionalization agent was 3-aminopropyltriethoxysilane 99% with the linear formula of ($C_9H_{23}NO_3Si$) which prepared from Sigma-Aldrich (3050 Spruce Street, Saint Louis, USA). Epoxy resin was an undiluted clear dysfunctional bisphenol A, Epon 828 purchased from Shell Chemicals Co. with epoxide equivalent weight 185–192 g/eqiv and the solvent was Tetrahydrofuran (THF) with purity (GC) more than 99% provided from a German company named Merck Co. The isotactic PP was supplied from Bandar Imam Petrochemical Co. (Iran) with the melt flow index of 8 g/10 min and density of 0.902 g/cm3. And powder form of poly (vinyl chloride) with K value of 65 was purchased from Bandar-e-Emam petrochemical company, Iran.