Synthesizing Iron Atom Doped Carbon Nanotubes

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ABSTRAK

Salah satu tantangan utama dalam menyintesis nanokomposit karbon *nanotube* (CNT) yang didoping gugus besi berbasis *polytetrafluoroethylene* (PTFE) adalah mencapai doping yang seragam tanpa menyebabkan agregasi atau pemisahan fasa gugus besi, yang dapat berdampak buruk pada sifat material. Nanopartikel besi cenderung menggumpal karena interaksi magnetiknya yang kuat dan energi permukaannya yang tinggi, menghasilkan doping yang tidak homogen yang mengurangi keefektifan komposit dalam aplikasi seperti pelindung elektromagnetik, katalisis, atau penyimpanan energi. Untuk mengatasi hal ini, teknik sintesis terkontrol seperti *Chemical Vapor Deposition* (CVD) dengan laju aliran prekursor yang diatur atau metode berbasis larutan dengan surfaktan dapat digunakan. Karakterisasi yang akurat menggunakan analisis SEM-EDX juga sangat penting, meskipun membedakan gugus besi dari matriks karbon bisa jadi sulit karena tingkat kontras yang serupa. Teknik pelengkap seperti mikroskop elektron transmisi (TEM) atau spektroskopi fotoelektron sinar-X (XPS) dapat memberikan wawasan struktural yang lebih rinci.

Kata kunci: *polytetrafluoroethylene (PTFE), iron cluster-doped carbon nanotubes (CNT), nanocomposite synthesis, Chemical Vapor Deposition (CVD), SEM-EDX analysis, electromagnetic shielding.*

ABSTRACT

One of the main challenges in synthesizing polytetrafluoroethylene (PTFE)-based iron cluster-doped carbon nanotube (CNT) nanocomposites is achieving uniform doping without causing aggregation or phase separation of the iron clusters, which can adversely affect the material's properties. Iron nanoparticles tend to agglomerate due to their strong magnetic interactions and high surface energy, resulting in inhomogeneous doping that diminishes the effectiveness of the composite in applications like electromagnetic shielding, catalysis, or energy storage. To mitigate this, controlled synthesis techniques such as Chemical Vapor Deposition (CVD) with regulated precursor flow rates or solution-based methods with surfactants can be utilized. Accurate characterization using SEM-EDX analysis is also crucial, although distinguishing iron clusters from the carbon matrix can be difficult due to similar contrast levels. Complementary techniques like transmission electron microscopy (TEM) or X-ray photoelectron spectroscopy (XPS) can provide more detailed structural insights.

Keywords: *polytetrafluoroethylene (PTFE), iron cluster-doped carbon nanotubes (CNT), nanocomposite synthesis, Chemical Vapor Deposition (CVD), SEM-EDX analysis, electromagnetic shielding.*

1. INTRODUCTION

The effect of high energy (up to10^{20} eV) fluxes of space charges (electrons and ions) on the material and equipment of spacecraft, as well as the spacecraft crew, may cause a failure of space missions. The problem can be solved by development of novel materials that are exceedingly resistant to radiation along with mechanical, thermal, electrical, and optical features required for space missions. Therefore, composite materials are considered as the most promising ones. Composite materials are composed of a number of materials with different properties. The properties of the created composite material depend on the chemical composition of the constituents, their sizes, size distributions and shapes as well as the orientations in the matrix. The properties of the created composite will be different from the characteristics of its components.

The nanocomposites demonstrated better mechanical, thermal and physical properties because the nanosize fillers (nanotubes, graphene ribbons, metallic and nonmetallic nanoparticles, and nanofibers and nanofilms) imbedded in a matrix material (polymers, metals, alloys, glass, ceramics) have a large specific surface area, which leads to a considerably extended volume of interphase boundaries between the filler and matrix. Carbon nanotubes (CNTs) are considered as durable and lightweight fillers for nanocomposites. According to Ajayan et al. (2003) [1], the excess surface energy of fillers and the stress accumulated at these boundaries lead to a broken interphase equilibrium and affect the final structure and properties of a nanocomposite. In this case, the features of the interface area between the filler and matrix can be significantly different from the properties of the matrix material. The nanocomposite properties will depend on the distribution of the filler in the matrix.

Carbon nanotubes (CNTs) are well-thought-out as a sustainable material for the next generation energy efficient systems, solar cells, fast-charging batteries, etc. During his study on synthesis of fullerenes Iijima (1991) [2] first observed the existence of carbon nanotubes. Carbon nanotubes became of interest for their electrical, thermal and mechanical properties and predominantly for nanoelectronics. Carbon nanotubes are considered as a potential high conductive and energy efficient interconnect material to replace conventional metal conductors (e.g. copper) for integrated circuits. Due to their special Dirac energy band structure carbon nanotubes have a semiconducting or conducting property. Nevertheless, the chirality of CNTs can’t be controlled and more research is needed to understand its mechanism.

Recently, an application of inorganic nanotubes doped with other chemical elements (silicon, metals, metal oxides, etc.) has become more attractive (Ivanovskii, 2002; Golberg et al., 2007a) [3, 4]. Doping CNT with conducting atoms or atom clusters could be one of the solutions to evade its uncertain conducting or semiconducting behavior. Ayala et al. (2010) [5] suggested that a modification of the crystalline CNT by creating defects or doping with foreign atoms brings a tunable energy band structure, and then a shift of Fermi-energy level could help to enhance the electrical properties of CNTs.

Glerup et al. (2007) [6] theoretically showed that the conduction in CNT occurs via the delocalized π-electron system. At room temperature, both metallic and semiconducting undoped single walled carbon nanotubes (SWCNT) are ballistic conductors conducting channels. In order to have more transport channels, which means involve higher energy bands beyond the first π-bands, requires huge electron excitation energy in the order of 1eV, equivalent to the temperature about 1200 K, which is not possible for practical applications. Thus, tuning the energy band gap becomes the key point that can be modified by doping external atoms in order to create extrinsic electron states.

The studies show that the radiation effects on nanostructures and materials produced on their basis differ in comparison with similar effects in micro and macro sized objects. The interaction between a nanostructure and the high energy space radiation transfers a very small portion of the energy of the affecting particle. Therefore, a nanosize object can involve a small number of arising additional carriers of charge or structural defects (Voronina et al., 2011) [7]. Because of the rough surfaces of nanotubes, a considerable number of the atoms displaced from the nodes of hexagonal cells exit them without interacting with other atoms, also reducing the number of radiations induced defects in the nanotubes (Voronina et al., 2011) [7]. In irradiated multilayer nanotubes the displaced atoms will be absorbed into the space between layers, generating additional bonds. Similar processes also occur in aggregated nanotubes as a result of interaction between nanotubes. The mechanical and electrical properties of such aggregations will be improved because of this (Krasheninnikov and Nordlund, 2010) [8]. CNTs also have the ability to heal defects, which increases their radiation durability. This effect is that the vacancies arising in hexagonal cells are transformed, moving to the equilibrium state with minimum energy (Voronina et al., 2011) [7]. Moreover, some of the carbon atoms displaced from nodes can be captured by CNT surfaces and migrate on them, eliminating vacancies when they recombine with migrating atoms. For quite high absorbed doses, the structure of nanotubes begins to break and they become amorphous (Krasheninnikov and Nordlund, 2010) [8].

Boron nitride (BN) is another potential material to be used in aerospace technology. The structure of these boron nitride nanotubes (BNNTs) is similar to CNTs. The model description of BNNTs allows them to be visualized as cylindrically curved sheets of hexagonal boron nitride (*h*-BN) (Golberg et al., 2007b) [9]. However, all bonds in CNTs are covalent, while in BNNTs they are to some extent ionic due to the nonuniform distribution of electrical charge between the boron and nitrogen atoms. This could explain the rare occurrence of single layer nanotubes among BNNTs (Golberg et al., 2007b) [9]. Multilayer BNNTs have an internal structure that is very similar to that of multilayer CNTs, although the bonds between layers should be more durable than in CNTs. BNNTs have high mechanical durability at low densities; also, their thermal conductivity is quite satisfactory and their thermal resistance is higher than that of CNTs, which is important when using such nanotubes and nanotube based composites in aerospace technology (Golberg et al., 2007b) [9]. Unlike CNTs, BNNTs are characterized by a rather wide energy gap (around 5.5 eV) that is independent of tube chirality; i.e., BNNTs are dielectrics (Oku et al., 2008) [10]. BNNTs also exhibit great stability to oxidation, as compared to CNTs (Chen et al., 2004) [11]. The experimental data obtained by irradiating nanotubes with electrons having energies of 200 keV show that multilayer BNNTs are more resistant to radiation than multilayer CNTs (Celik-Aktas et al, 2007; Lehtinen et al., 2010) [12, 13].

Voronina et al. (2011) [7] compared carbon nanotubes (CNTs) with boron nitride nanotubes (BNNTs) as fillers enable them to construct polymer nanocomposites with the characteristics required for aerospace technology. It is shown that the properties of polymer nanocomposites depend on nanotube dispersion in the matrix, which is determined by the ratio of interaction forces between the nanotubes themselves and their interaction with polymer units. Also, it is suggested that BNNT fillers are preferable in order to increase the radiation hardness of nanocomposites and construct radiation shields. CNTs interact with one another only through Van der Waals forces, while BNNTs involve additional electrostatic forces due to the nonuniform charge distribution on the surface of tubes, which can considerably affect the interaction energy. The threshold energy for atoms to escape from nanotube walls during irradiation depends on their structure, diameter, and composition. Moreover, it increases with an increase in nanotube diameter. Furthermore, the structural radiation induced defects are different for CNTs and BNNTs. Thus, in CNTs, irradiation leads to the formation of mainly single and double vacancies, and to adsorbed atoms and Stone–Walles defects consisting of two pentagons and two heptagons. However, in BNNTs, triangular vacancies resulting mainly from the removal of boron atoms predominate in the case of electron irradiation. The radiation hardness of nanotubes can be increased by healing structural defects through the relocation of displaced atoms on the surface and their recombination with emerging vacancies.

Novikov et al. (2014) [14] showed that the carbon nanotubes resist formation and accumulation of radiation defects due to the fact that a large fraction of escaped carbon atoms leave the nanostructure without collision with other atoms. The defects will be healed by rebuilding of broken bonds and recombination of atoms and vacancies migrating over the surface. The efficiency of recombining the displaced atoms with vacancies will increase because they are caught by the interface. The properties of nanocomposites significantly depend on the homogeneous distribution of the embedded particles in the polymeric matrix.

There are some ideas that the doping atoms must preferably be neighboring to the carbon atom from the periodical table (e.g. nitrogen, boron) with one more and less valence electron, in order to create N- and P- type doping respectively. Paez (2006) [15] showed that an incorporated nitrogen in CNT will be in the states above the Fermi-energy level. As the nitrogen ionizes, the escaped electrons will fill empty states at the edge of the valence band and an N-type semiconducting CNT will be formed. The Fermi-energy level of the nanotube will move upwards in energy and position itself at the nitrogen states in the density of states. Contrariwise, for the boron doping, due to the one less valence electron, boron can act as electron traps for delocalized π-electron. If these traps are occupied (the boron states are ionized), the Fermi-energy level will move downwards in energy towards the valance band. Both processes will reduce the semiconducting CNT energy gap and enhance the conducting behavior of CNT.

Some researchers tried to model CNT as an RLC electrical circuit (Srivastava and K. Banerjee, 2005; Todri-Sanial et al., 2016; Todri-Sanial, 2016) [16-18]. The RLC electrical model has been used by other researchers to create analytical formulas to describe the CNT's conductivity behavior. For example, Liang et al. (2016) [19] considered the physical resistance model and simulated the conductance of both undoped and N-doped single walled CNTs. CNTs were considered as a quantum wire transport where the conductance is estimated using the two-terminal Landauer-Buttiker formula. With N number channels in parallel, the conductance is defined as:

$$G = \frac{Ne^2 T}{h} \tag{1}$$

where T is the transmission coefficient for electrons passing through the CNT. Each CNT has four conducting channels in parallel ($N=4$) due to electron spin degeneracy and two effective atoms per unit cell. A scattering resistance becomes significant for the length of CNT greater than the mean free path (L_{mfp}). Then the total resistance is defined as (Liang et al., 2016) [19]:

$$R_{CNT} = \frac{h}{2Ne^2}\left(1 + \frac{L}{L_{mfp}}\right) + R_C \tag{2}$$

where R_C is the contact resistance for interconnect; L_{mfp} is the mean free path determined as (Jiang et al., 2001):

$$L_{mfp} = \frac{D\sqrt{3}\psi^2}{2\sigma_\varepsilon^2 + 9\sigma_\psi^2} \tag{3}$$

where D is the diameter of CNT; ψ , σ_ε and σ_ψ are tight-binding calculation parameters. For undoped CNT: $\sigma_\varepsilon = 0.04\ eV$ and $\sigma_\psi = 0$; for doped CNT: $\sigma_\varepsilon = 0$ and $\sigma_\psi = 0.06\ eV$ (Jiang et al., 2001) [20].

Liang et al. (2016) [19] investigated the carbon nanotubes (CNT), wrapping a 2D graphene sheet to form a 1D carbon structure. The authors studied the fundamental physics of doped CNTs and described how doping changes the electrical property of CNTs. Electrical property of doping CNT was explained physically by a modification of hybridization, which is a chemical concept describing a mix of atomic orbitals with shared electrons under different energies and shapes to form chemical bonds. It is suggested that adding external different atoms will change the lattice strength and surface roughness of the doping material. Doping with a donor atom could increase delocalized electrons in the system in order to give more charge carriers for current transport. Also an acceptor atom doped in the system will create a localized vacuum site enhancing the electron mobility. In a CNT each atom has 4 valence electrons, three of these electrons participate in the C-C sigma bonding but one of them occupies a Pz orbital forming delocalized electron states with a range of energies that include the Fermi-energy. These states are in control of the electrical conductivity of carbon nanotubes. The paper also provides analytical models and simulation results on CNT conductance variation for N-type doped CNTs. Simulation results show that doping can reduce overall CNT resistance by 89%.

The RLC electrical model has been applied for multi walled carbon nanotubes (MWCTs) as well (Burlon et al., 2004; Li et al., 2008) [21, 22]. The MWCNTs will have much more parallel conducting channels. Therefore, the MWCNTs have a smaller resistance. The resistance decreases with longer MWCNT lengths and a large number of shells.

Recently, carbon nanotubes (CNTs) doped with metallic elements have been widely attracted the attention of researchers due to their functional properties. For example, studies have shown that the transition metal doping on intrinsic CNTs can break the original electronic balance of CNTs and promote the interaction between CNTs and some gases (Yoosefian and Etminan, 2016) [23]. In addition, constructing vacancy defects on the surface of CNTs would create dangling bonds and raise the electron activity at the defect sites of CNTs, thus elevating the sensitivity of CNTs to gases (Lee et al., 2005) [24]. It is well known that CO poisoning to human beings is largely due to the closer affinity of CO with hemoglobin than O_2. Solid combination of CO with Fe^{2+} in hemoglobin makes the oxygen-carrying ability of hemoglobin decrease sharply, leading to body hypoxia and gas poisoning (Fu et al., 2017) [25]. Therefore, doping Fe on CNTs may significantly improve their sensitivity to CO and Fe-doped CNTs can be used as next-generation CO sensing materials. It has been demonstrated that CNTs doped with Au, Ag and Pt can detect NO_2, NH_3, O_2 and some other gas molecules with faster response and larger detection range than other existing gas sensitive materials (Zhao et al., 2001; Lin et al., 2013; Barberio et al., 2014) [26-28].

The change of electrical conductivity of CNTs after the adsorption of CO was observed (Liu et al., 2019) [29]. Theoretical study showed that, after CO adsorption, the fundamental reason resulting the change of electrical conductivity of CNTs was that the charge transfer amount between CNTs and CO was over 0.1e, which would alter the band structure and density of states (DOS) of the adsorption system, and finally change the electrical conductivity of the system (Jhi et al., 2000) [30]. Computations of the adsorption of CO molecules on Fe-doped single-vacancy-defected carbon nanotubes (Fe-SV-CNTs) show that the interaction of Fe-SV-CNTs with CO, although is slightly weaker than that of Fe-doped intrinsic CNTs, is much stronger than that of intrinsic CNTs and single-vacancy defected CNTs (SV-CNTs) (Liu et al., 2019) [29]. After CO adsorption, the electrical conductivity of Fe-SV-CNTs has a much more significant change than that of other types of CNTs.

There are various approaches to model effective thermal, electrical and mechanical properties of composites with embedded particles. Felske (2004) [31] developed the self-consistent field model, an analytical solution for the effective conductivity of a medium in which composite spheres are randomly distributed throughout a continuous phase. The composite spheres are taken to have a homogeneous core surrounded by a homogeneous spherical shell of a thermally different material. A contact resistance exists between the outer surface of the shell and the continuous medium in which it is embedded. The present result extends previous studies which considered such spheres to be homogeneous.

Voronina et al. (2011) [7] studied the structural features of nanotube based polymer nanocomposites and described the specifics of radiation impact on nanostructures. Mathematical modeling has been used to investigate mechanisms of the generation of radiation induced defects in nanotubes, nanotube dispersion in polymers, and the absorption of radiation fluxes by some nanocomposites.

Analytical model of the dielectric material with embedded nanoparticles doped with conductive atom clusters (the core-shell structure of Fe@CNT nanocomposite) containing the interphase space charges has been developed by Bakhtiyarov and Ferguson (2020) [32]. A combined solution of the permittivity equation of the heterogeneous system with the Gauss-Codazzi and the electric potential continuity equations is allowed to simulate the relative permittivity of the composite dielectric material as a function of the concentration of the embedded nanoparticles, as well as the space charge content. The simulations for the Polytetrafluoroethylene (*PTFE*) dielectric material with embedded carbon nanoparticles doped with Fe atom clusters showed that the relative permittivity of the *PTFE* nanocomposite increases with increasing the amount of the embedded CNPs doped with Fe clusters and the charge content. In absence of embedded CNPs the solution reduces to the Maxwell-Garnett equation.

The latest studies show that the thermo-mechanical and tribometric properties of polymer materials can be improved by introducing certain modifiers (fillers) in the polymer matrix (Rukhadze et al., 2010a, 2010b; Kutelia et al., 2018a, 2018b, 2020, 2021) [33-38]. Several types of fillers were tested for PTFE based composite in these studies, such as, oxides, borides, carbides, nitrides and micro- and nano powders of different materials in the form of particles of different morphology, size and composition. For example, a considerable increase of the wear resistance was achieved by introducing micro and nanoparticles, which play a role of a wear inhibitor for the transient film formed during a friction. However, these additives didn’t increase the strength of the material.

2. METHOD

The preparation of PTFE (Polytetrafluoroethylene) + Fe cluster-doped CNT (carbon nanotube) nanocomposites involves several key steps: synthesizing Fe cluster-doped CNTs using a chemical vapor deposition (CVD) process with iron catalysts, purifying the CNTs to remove impurities, dispersing the CNTs in a solvent with techniques like ultrasonication to ensure uniform distribution, dissolving PTFE in organic solvents to facilitate mixing, blending the CNT dispersion with PTFE solution, casting the mixture into desired shapes and allowing solvent evaporation, followed by sintering or hot pressing to consolidate the material, and concluding with extensive characterization through methods like scanning electron microscopy (SEM), X-ray diffraction (XRD), and mechanical testing to evaluate the composite's structural integrity, dispersion of CNTs, and its thermal and mechanical properties.

The PTFE-based nanocomposites containing 10.0 wt.% of *CNTs* doped with *Fe* atom clusters were synthesized by the powder metallurgy method according to the procedure described by Kutelia et al. (2018a) [35]. A schematic of the main steps of the synthesizing process of PTFE + Fe cluster-doped CNT nanocomposite is shown in Figure 1. A commercial *PTFE* micro-powder of 2,200 kg/m^3 density and 0.5 - 5 µm grain size was used for preparation of the bulk specimens. The synthesis of mono- and bimodal magnetic carbon nanopowders composed of *Fe* atom cluster-doped *CNTs* as filler for the *PTFE* matrix was performed in two different modes using single- and double-zone ethanol vapor pyrolysis experimental setups described by Kutelia et al. (2018b, 2018c) [36, 39] and Rukhadze et al. (2018b) [34].

3. RESULTS AND DISCUSSION

SEM-EDX analysis allows for a detailed examination of the nanocomposite’s morphology and elemental composition, where SEM reveals the surface structure, size, and distribution of carbon nanotubes (CNTs) within the PTFE matrix, while EDX provides elemental identification and quantitative analysis, ensuring the presence and uniform distribution of Fe clusters and other dopants, as well as offering elemental mapping to visualize the spatial arrangement of these components throughout the composite.

Before preparing the mixtures of different compositions, randomly selected samples of the nanopowders were examined by *SEM-EDX* analysis in order to determine morphology, sizes, aspect ratios and a composition of the particles. Figures *2a-2d* show *SEM* images and the respective *EDX* spectra of mono- (Figures *2a* and *2b*) and bimodal (Figures *2c* and *2d*) *CNTs* doped with *Fe* atom clusters, which will be used as a filler for manufacturing PTFE-based nanocomposite material. As seen from these figures, the monomodal nanopowder in a free-poured state consists of iron-doped CNTs of practically the exact sizes and morphology (less than 1 µm long and ~ 200 nm diameter) where atomic iron clusters are mainly located at one end (inlet) of CNTs (Figure 2a). However, the bimodal filler nanopowder consists of Fe atom cluster-doped CNTs with diameters of submicron and nanometers (Figure 2c). Therefore, the average weight concentration of iron in the bimodal nanopowder is ~2.5 times higher than that in the mono-modal filler (compare Figure 2b with Figure 2d).

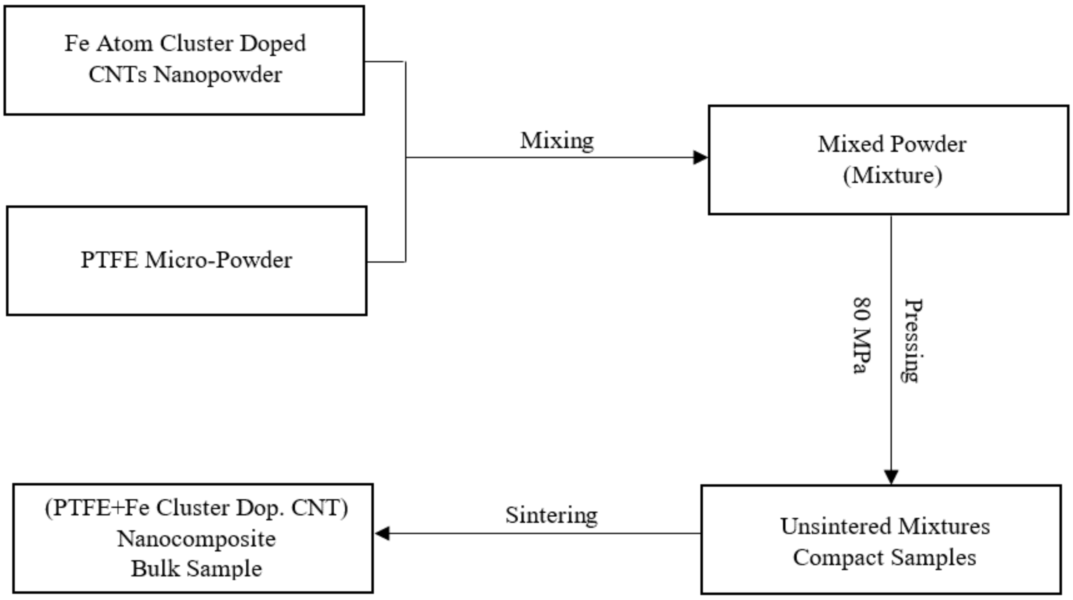

Figure 1. The Schematics of Main Steps of The Preparation Process of PTFE + Fe Cluster-Doped CNT Nanocomposite

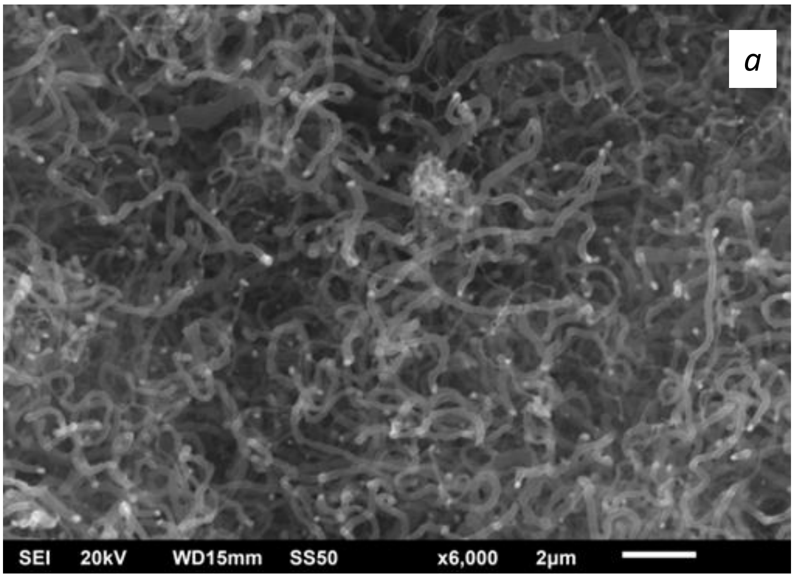

Figure 2a. ***SEM*** **Images Spectra of Mono Atomic, Iron Clusters Located at One End (Inlet) of CNTs**

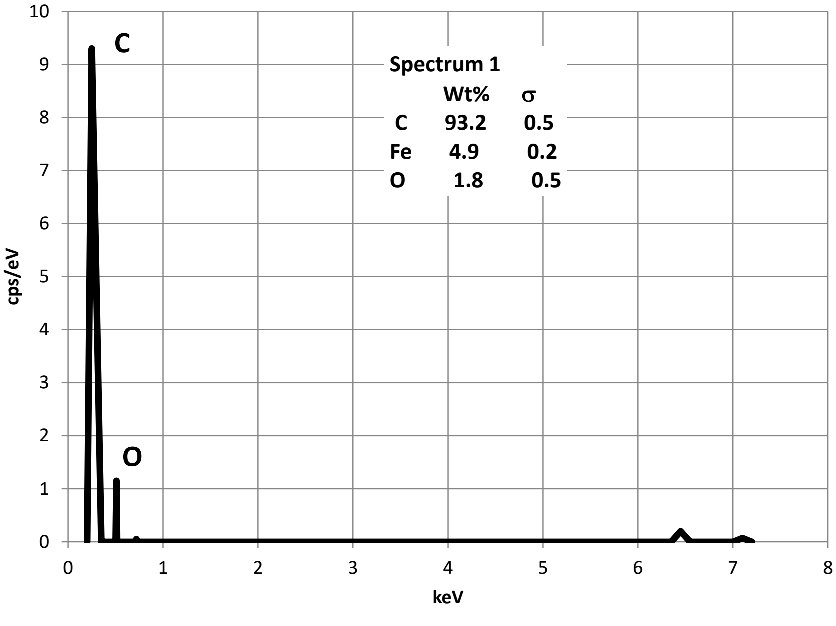

Figure 2b. The Respective ***EDX*** **Spectra of Mono Atomic, The Average Weight Concentration of Iron in The Mono-Modal Filler**

Figure 2 provides a comprehensive visual representation of the morphology and composition of both mono- and bimodal Fe atom cluster-doped carbon nanotube (CNT) nanopowders, which are employed as fillers in the production of PTFE-based nanocomposites. Panels (a) and (b) showcase scanning electron microscope (SEM) images and energy-dispersive X-ray (EDX) spectra of the mono-doped CNTs, highlighting their structural characteristics, particle sizes, and elemental distribution. In contrast, panels (c) and (d) present the corresponding SEM and EDX data for the bimodal doped CNTs, allowing for a comparative analysis between the two types of CNTs. The SEM images reveal the fine morphology of the CNTs, with a clear distinction in their surface features, while the EDX spectra provide insights into the elemental composition, confirming the successful doping of Fe clusters. These detailed analyses are essential for understanding the influence of the doping process on the physical properties of the CNTs and their subsequent impact when used as a filler in PTFE-based nanocomposites, particularly in terms of enhancing the material's mechanical, thermal, and electrical properties.

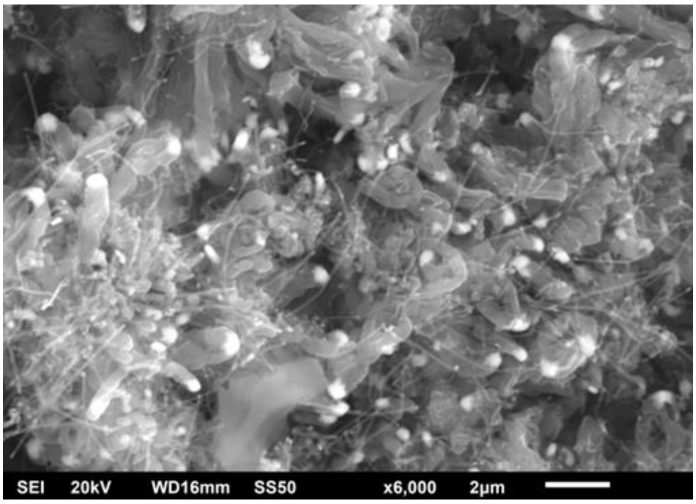

Figure 2c. ***SEM*** **Images Spectra of Bimodal, The Bimodal Filler Nanopowder Consists of Fe Atom Cluster-Doped CNTs with Diameters of Submicron and Nanometers**

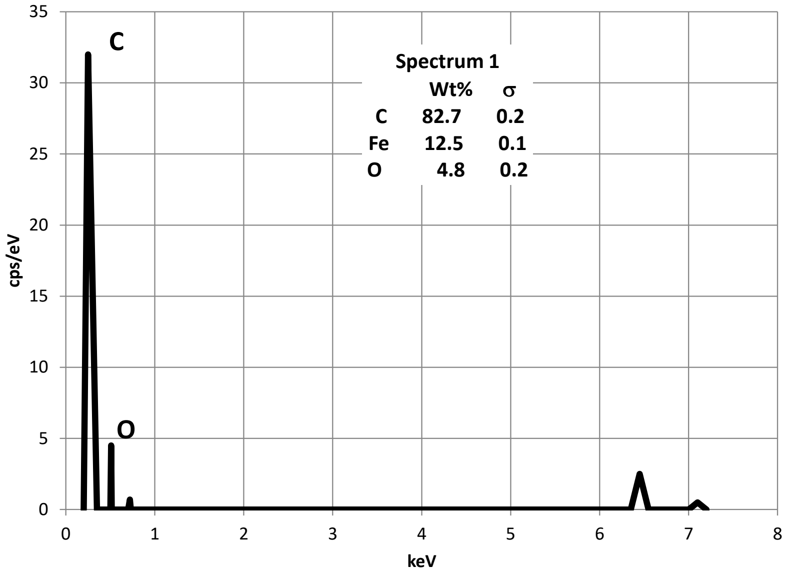

Figure 2d. The Respective ***EDX*** **Spectra of Bimodal, The Average Weight Concentration of Iron in The Bimodal Nanopowder ~2.5 Times Higher than Mono-Modal Filler**

4. CONCLUSIONS

Different techniques of synthesizing and modeling of different elements doped carbon nanotubes are reviewed. A new procedure of the synthesizing process of Polytetrafluoroethylene (PTFE) based iron cluster-doped carbon nanotubes nanocomposite is described. To analyze morphology, sizes, aspect ratios and a composition of the particles, the SEM-EDX techniques have been used and the results are presented.

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