

# Impact of nanocomposite material to counter injury in physical sport in the tennis racket

Hao Jin<sup>1</sup>, Bo Zhang<sup>2</sup> and Xiaojing Duan<sup>\*3</sup>

<sup>1</sup>Department of Sports Work, Hebei Agricultural University, Baoding 071000, Hebei, China

<sup>2</sup>Department of Physical Education and Teaching, Hebei Finance University, Baoding 071000, Hebei, China

<sup>3</sup>Department of Functional Ultrasound, Affiliated Hospital of Hebei University, Baoding 071000, Hebei, China

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**Abstract.** Sports activities, including playing tennis, are popular with many people. As this industry has become more professionalized, investors and those involved in sports are sure to pay attention to any tool that improves athletes' performance. Tennis requires perfect coordination between hands, eyes, and the whole body. Consequently, to perform long-term sports, athletes must have enough muscle strength, flexibility, and endurance. Tennis rackets with new frames were manufactured because tennis players' performance depends on their rackets. These rackets are distinguished by their lighter weight. Composite rackets are available in many types, most of which are made from the latest composite materials. During physical exercise with a tennis racket, nanocomposite materials have a significant effect on reducing injuries. Materials as strong as graphite and thermoplastic can be used to produce these composites that include both fiber and filament. Polyamide is a thermoplastic typically used in composites as a matrix. In today's manufacturing process, materials are made more flexible, structurally more vital, and lighter. This paper discusses the production, testing, and structural analysis of a new polyamide/Multi-walled carbon nanotube nanocomposite. This polyamide can be a suitable substitute for other composite materials in the tennis racket frame. By compression polymerization, polyamide was synthesized. The functionalization of Multi-walled carbon nanotube (MWCNT) was achieved using sulfuric acid and nitric acid, followed by ultrasonic preparation of nanocomposite materials with weight percentages of 5, 10, and 15. Fourier transform infrared (FTIR) and Nuclear magnetic resonance (NMR) confirmed a synthesized nanocomposite structure. Nanocomposites were tested for thermal resistance using the simultaneous thermal analysis (DTA-TG) method. scanning electron microscopy (SEM) analysis was used to determine pores' size, structure, and surface area. An X-ray diffraction analysis (XRD) analysis was used to determine their amorphous nature.

**Keywords:** compression polymerization; nanocomposite; PA/MWCNT; physical exercise; polyamide; tennis racket

## 1. Introduction

With the advancement of nanotechnology, new opportunities have opened up for making intelligent materials that fit the needs of athletes while also providing the highest level of safety and comfort to help them perform at their best (Young and Liu 2016b). The industry has grown significantly recently as it has developed new methods for manufacturing composite materials, systems, and devices (Farsi *et al.* 2012). The use of composites is increasing for various reasons (Chen 2022). Nevertheless, composite products are robust and lighter, which is why they are prevalent (Rusu and Onciu 2005). Nanotechnology is used in sports for the first time with tennis rackets as a symbol of sports equipment (Kannan *et al.* 2021). Sports equipment, including tennis rackets, has evolved with different materials and many innovations being introduced (Peng *et al.* 2019). Only a few materials, however, had a long-term impact on the racquet frame due to its simplicity and functionality. Like many other products, choosing materials for tennis racket frames began with wood,

considered the most common material for centuries (Harifi and Montazer 2015). Manufacturers took several hundred years to produce metal racket frames (Wang and Wang 2014). However, metal frames were never able to hold the market for long as wooden rackets, and in fact, the emergence of composite rackets killed the development of metal rackets (Tang *et al.* 2013). A famous sports equipment manufacturer, Wilson, has designed and made rackets that are 22% more powerful and almost two times more stable than typical rackets (Cibo *et al.* 2020). With these features, players can perform faster, which is crucial in this game (Ji 2012, Li and Cheng 2013). Also, Wilson is trying to improve the existing tennis balls, Tennis injuries typically involve the shoulder, elbow, and wrist. In addition, lower limb injuries, such as knee and ankle injuries, are common due to the high speed of this sport and the sudden changes in the direction of movement of the athlete (Xu 2021, Wen 2022). Using rackets made of nanocomposites helps fix the injuries associated with this sport (Miteva 2021). With the development of lighter and stronger materials, tennis rackets are becoming more assertive, and players are becoming more maneuverable (Shang *et al.* 2013). As a result of material control at the molecular level, the ball moves straight, increasing the accuracy of the athlete's shots. In modern tennis rackets, most materials are carbon fiber-based composites reinforced with other materials,

\*Corresponding author, Ph.D.,  
E-mail: cmwn@163.com

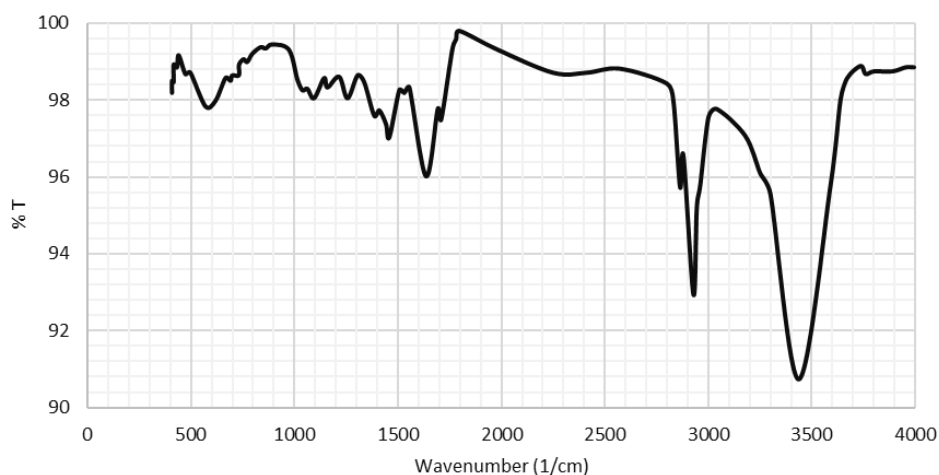


Fig. 1 Image from FT-IR of PA/MWCNT 10 wt% nanocomposite

including polyamides (Ramírez-Herrera *et al.* 2016, Alexandrescu *et al.* 2017).

Nylons and aliphatic polyamides are the most crucial engineering polymers within the polyamide family (Bisoi *et al.* 2017). As an engineering plastic, this polymer is a thermoplastic polymer (Sheng *et al.* 2021, Si *et al.* 2021). This polymer has good properties of abrasion resistance, chemical stability, and high toughness (Hsiao *et al.* 2015). Engineered plastics such as polyamides and nylons are formed by compression polymerization of diamines and bifunctional acids or polymerization of amino acids (Zhang *et al.* 2019). A significant disadvantage of nylon is that, due to the characteristic of most polymers, they exhibit weak electrical properties, and their electrical permeability is very low (Mitiakoudis and Gandini 1991). They accumulate an electric charge on their surface when exposed to electric fields. It becomes much more critical when our polymer is supposed to come into contact with flammable materials (Rezania *et al.* 2019). An electrically conductive nanoparticle, such as a carbon nanotube, can be used to solve this problem. This material has a higher electrical conductivity than nylon, making it possible to prevent the accumulation of electrical charge on the surface of the polymer matrix (Yuan *et al.* 2018). Because the carbons in the nanotubes are SP<sup>2</sup> hybridized, the electron cloud on the carbons gives the nanotubes excellent electrical properties. Consequently, adding nanotubes to a polymer matrix can improve electrical properties (Sahoo *et al.* 2010, Rahmat and Hubert 2011). A nylon fiber's strength and hardness make it an excellent material for products such as ropes, safety belts, parachutes, and tennis rackets (Ates *et al.* 2017). As a result, nanotechnology has been proven to have practical applications in sports, including sports textiles and clothing, sports equipment, and even medical equipment for athletes (Young and Liu 2016a).

## 2. Results and discussion

Using N-Methyl-2-pyrrolidone (NMP) solvent, Triphenylphosphine (TPP), and pyridine as condensation reagents, polyamide is formed by direct condensation of terephthaloyl

chloride monomer and aromatic naphthalene-1,5-diamine. Ultimately, 85% of the precipitate was obtained. Identifying and detecting polyamide's chemical composition was possible using FT-IR diagnostics. Peaks at 1738 cm<sup>-1</sup> (asymmetric stretching vibration C=O), 1725 cm<sup>-1</sup> (symmetric stretching vibration C=O), 1375 cm<sup>-1</sup> (stretching vibration C-N) and 1227 cm<sup>-1</sup> (stretching vibration C-O-C) appear. The appearance of the peak in the region of 3275 cm<sup>-1</sup> is related to the stretching vibrations of the N-H group, and the peak in the region of 2925 cm<sup>-1</sup> is related to the stretching vibrations of aliphatic C-H (Wang *et al.* 2021, Zhou *et al.* 2021a, b, Wu *et al.* 2022). It is present in NHCO, and the bending band of N-H is 1600 cm<sup>-1</sup>. An OH band emits vibrations in the 3426 cm<sup>-1</sup> and aliphatic C-H vibrations in the 2925 cm<sup>-1</sup>. These peaks indicate that polymer tissues contain carbon nanotubes (Fig. 1).

MWCNT nanotubes and associated nanocomposite containing 5% MWCNT were also studied using XRD. Fig. 2, Fig. 3, and Fig. 4 illustrate the patterns produced by this analysis. Accordingly, the peak at  $2\theta = 27^\circ$  corresponds to graphite impurities in carbon nanotubes, while the peak at  $2\theta = 49^\circ$  corresponds to iron and nickel impurities. Moreover, for the pure polymer, the broad peak confirms the amorphous nature of the material. Nanocomposite samples containing 5% by weight of carbon nanotubes show characteristic peaks. The peaks at  $2\theta = 27^\circ$  and  $2\theta = 49^\circ$  indicate carbon nanotubes are present in this nanocomposite (Li *et al.* 2021, Si *et al.* 2021, Zhang *et al.* 2021, Wang *et al.* 2022a).

In the transmission electron microscope (TEM) image, no aggregation is observed, and relatively satisfactory dispersion of nanoparticles is observed, so it can be concluded that surface modification causes easier dispersion during the composite process (Yang *et al.* 2019, Du *et al.* 2022, Wang *et al.* 2022, Hu *et al.* 2023). Fig. 5 shows the TEM image of 5% PA/MWCNT nanocomposite.

SEM images of the hydroxylated carbon nanotubes in Fig. 6 depict a tube-like surface with a diameter of approximately 10 nm, indicating that the MWCNT-OH compound has a high surface area suitable to serve as a molecular template for the preparation of polymers.

The thermal properties of pure PA and PA/MWCNT

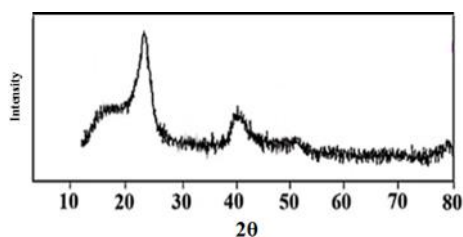


Fig. 2 X-ray image of MWCNT

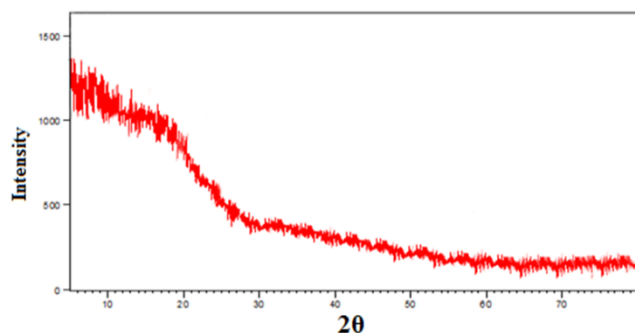


Fig. 3 Image of PA by X-ray

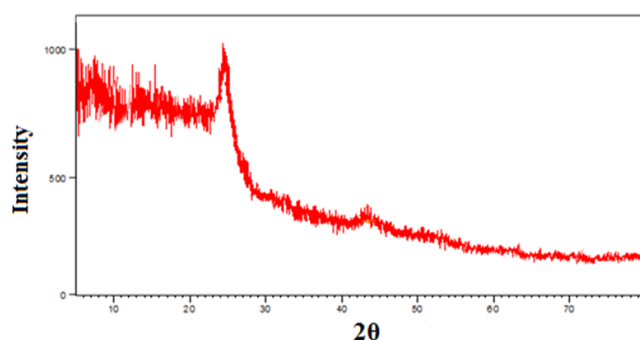


Fig. 4 Image of PA/MWCNT 5 wt% nanocomposite by X-ray

nanocomposites at 5 and 10 wt% were studied with Thermogravimetric Analysis (TGA) equipment under nitrogen atmospheres. Results are shown in Fig. 7. The results for these samples can be found in Table 1. Nanocomposites have been demonstrated to withstand temperatures of up to 300°C. In PA and PA/MWCNT nanocomposites with weight loss of 5 and 10% by weight, the weight loss temperature of 10% was recorded. In these nanocomposites, the residuals (character yields) exceeded 17 at 800°C. Because the polymer matrix is compatible with nanotubes, nanocomposites made from MWCNT have higher thermal stability. This combination of nanoparticles can improve the thermal resistance of nanocomposites.

### 3. Experimental

#### 3.1 Materials

Merck and Aldrich were used to supplying all reactants and were purified before use. Sigma-Aldrich supplied 1,5-dinitronaphthalene and terephthaloyl dichloride and

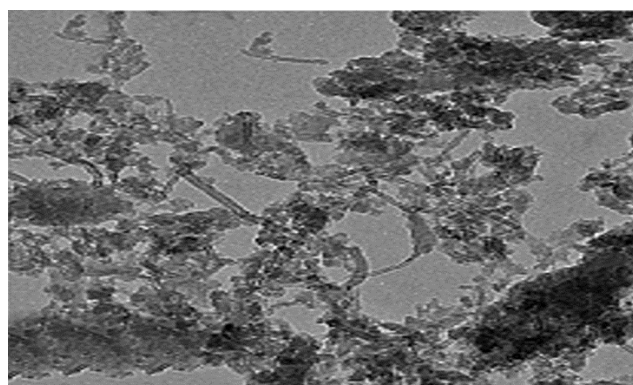


Fig. 5 Nanocomposite of 5% PA/MWCNT imaged using TEM

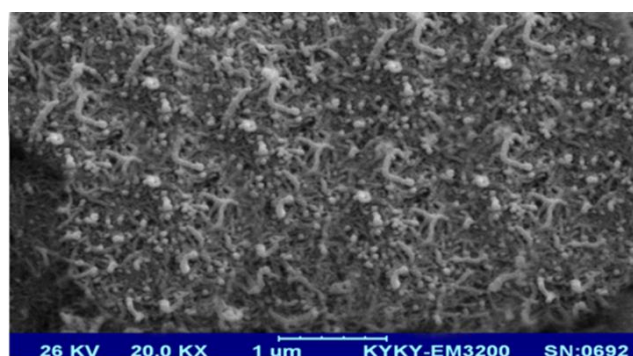


Fig. 6 Nanocomposite of PA/MWCNT imaged using FE-SEM

Table 1 PA/MWCNT nanocomposites and pure PA thermal properties

Sample	PA	PA/ 5%MWCNT	PA/ 10%MWCNT
T <sub>5</sub> <sup>a</sup>	210	250	301
T <sub>10</sub> <sup>b</sup>	236	368	320
Char Yield	18	15	10
LOI	21.8	22.9	20.1

<sup>a</sup>Under nitrogen atmosphere, at 10°C min<sup>-1</sup>, 5% weight loss was recorded by TGA.

<sup>b</sup>Under nitrogen atmosphere, at 10°C min<sup>-1</sup>, 10% weight loss was recorded by TGA.

recrystallized it before use. Merck provided triphenyl phosphite (TPP) for use without further purification. In order to purify NMP, it was distilled under reduced pressure over barium oxide (Omidi *et al.* 2013, Ebrahimi and Shafiei 2017, Ehyaei *et al.* 2017, Shafiei *et al.* 2019). Nitric acid and sulfuric acid (from Merck) were supplied as pure products. Neutrino (Iran) provided nano-sized Zn powder with an average particle size of 25 to 30 nm.

#### 3.2 Techniques

A Bruker Avance 400 MHz spectrometer was used for proton-nuclear magnetic resonance (1H NMR) analysis, and singlet (s) and multiplet (m) resonances were identified. In KBr powder, FT-IR products were measured using a Jasco-680 (Japan) spectrophotometer. To record X-ray diffraction

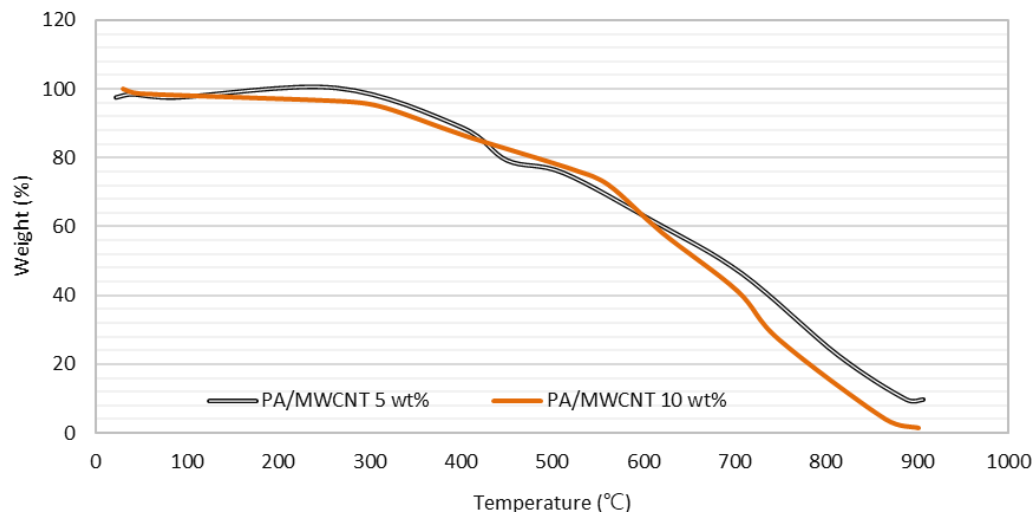
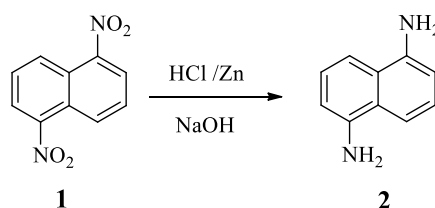
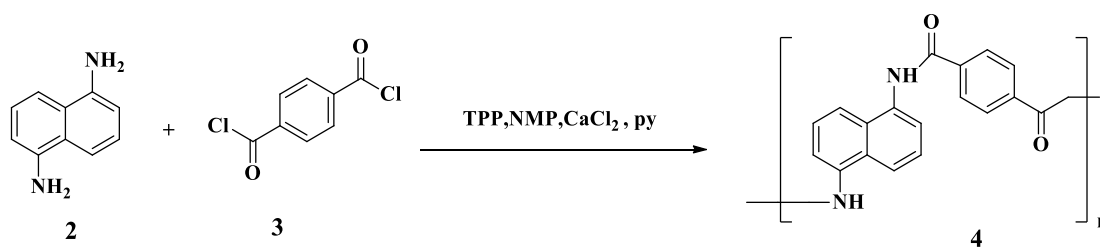


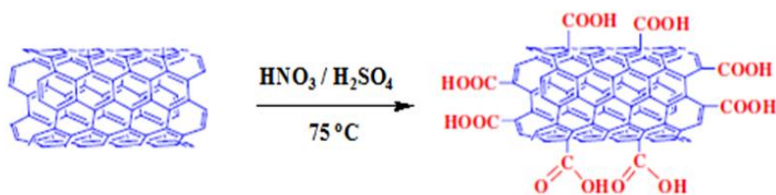
Fig. 7 An image of PA/MWCNT nanocomposites (5 and 10 wt %) taken with a TGA



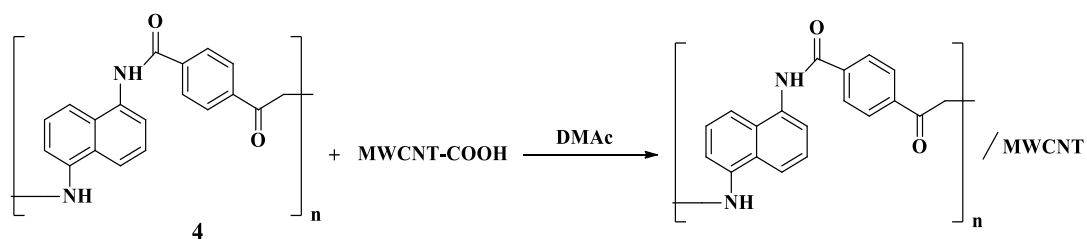
Scheme 1 A novel method for synthesizing naphthalene-1,5-diamine



Scheme 2 Using compression polymerization to prepare polyamides



Scheme 3 Method for preparing carboxyl functionalized MWCNT



Scheme 4 PA/MWCNT nanocomposites preparation method

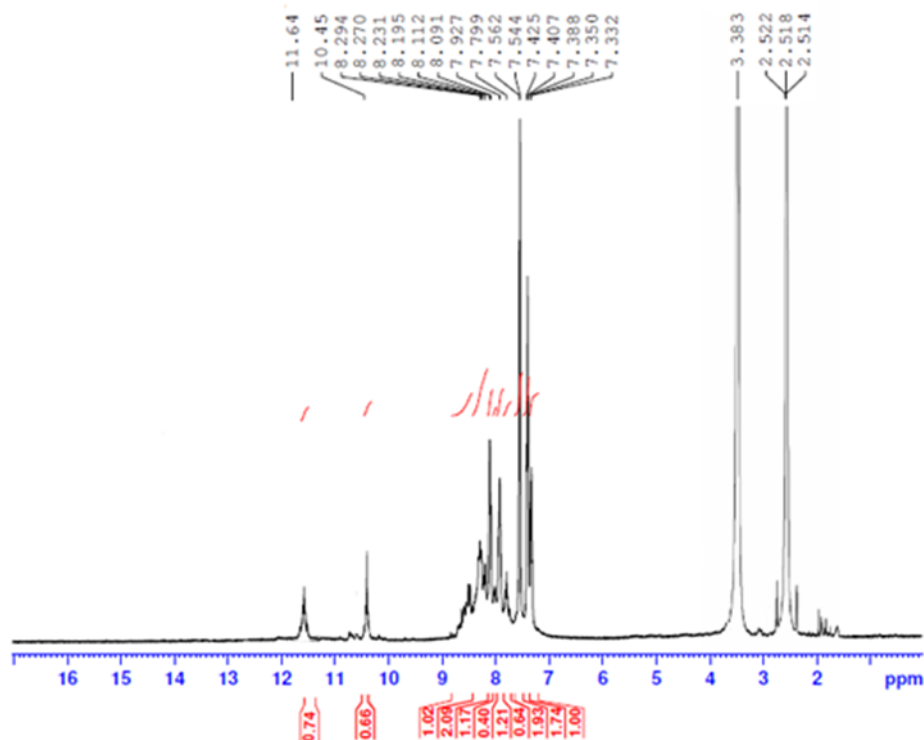


Fig. 8 PA/MWCNT 1H NMR spectrum

patterns, use a Bruker D8 Advance diffractometer. With a heating rate of 10°C per minute, the STA503 win TA can perform thermal gravimetric analysis (TGA) at temperatures from 25 °C to 800 °C under a nitrogen atmosphere. With the JEOL JEM-2000, the scanning electron microscope image was taken under a voltage of 20 kW and a working distance of 4 mm (Cao *et al.* 2022, Cheng *et al.* 2022, Wang *et al.* 2022b, Zhang *et al.* 2022).

### 3.3 An overview of monomer synthesis

#### 3.3.1 A novel method for synthesizing naphthalene-1,5-diamine

An acid solution of 0.1 g of 1,5-Dinitronaphthalene (1) in 0.4 mL of Hydrochloric acid (d. 1.18) was gradually mixed with 0.107 g of zinc dust, and the mixture was refluxed for one hour after the reaction subsided. Sodium

hydroxide solution was added to the reaction mixture to make it alkaline, and the precipitate was filtered, washed with water, and dried. A total of 0.08 g (81%) of Brown to Gray naphthalene-1,5-diamine (2) was obtained following the removal of the solvent (Scheme 1).

#### 3.4 Using compression polymerization to prepare polyamides

Add 0.057 g ( $3.1 \times 10^{-4}$  mol) naphthalene-1,5-diamine (2) to a 25 mL round-bottom flask, along with 0.1 g ( $3.1 \times 10^{-4}$  mol) terephthaloyl dichloride(3), 2 mL NMP, 0.06 g of  $\text{CaCl}_2$  and 0.3 ml of triphenyl phosphite were added. Then 0.5 ml of pyridine was added to the reaction mixture and stirred at room temperature for 30 minutes to mix the

reactants (Shafiei *et al.* 2016a, b, Mirjavadi *et al.* 2017c, Mousavi *et al.* 2017). The reaction mixture was refluxed at 110°C under a nitrogen atmosphere for 3 hours until a viscous mixture was obtained. After cooling, 50 ml of methanol was added to the flask's contents. The resulting precipitate was smoothed and dried. The produced polyamide (4) weighed 0.09 and had an efficiency of 85% (Scheme 2).

#### 3.5 Method for preparing carboxyl functionalized MWCNT

In most cases, covalent functionalization of MWCNT involves adding carbonyl and carboxyl groups through a mixture of  $\text{HNO}_3/\text{H}_2\text{SO}_4$ . In order to prepare carbon nanotubes, MWCNTs were first ultrasonicated for an hour in a 3:1 solution of nitric and sulfuric acids and then heated to 75°C using a magnetic stirrer (Ghadiri *et al.* 2016, Ebrahimi *et al.* 2017, Mirjavadi *et al.* 2017a, Mirjavadi *et al.* 2017b). A large amount of water was used to dilute the mixture after it had been refluxed for 8 hours, and then the nanotubes were separated using a centrifuge for 25 minutes. Sediment was separated from the acidic solution using membrane filters and vacuum pumps, then washed with deionized water until its pH reached 7. For 12 hours, it was heated to 65 °C and then dried. Carbon nanotubes with carboxylated functionalization are shown in Scheme 3.

#### 3.6 PA/MWCNT nanocomposites preparation method

For the first step, 3 ml of DMAc solvent was poured over 0.1 grams of prepared polyamide(4) and placed at 40

°C for 24 hours. Similarly, MWCNT-COOH was prepared in another balloon with 5%, 10%, and 15% weight percentages compared with the polymer substrate. For this purpose, 0.005, 0.01, and 0.015 grams of MWCNT-COOH were dissolved in 5 ml of DMAc solvent and stirred continuously by a magnetic stirrer for 24 hours at 40 °C. A subsequent step involved mixing the mixture with a polyamide solution and putting it at 40°C for one day and night, followed by a one-hour ultrasonic bath. The mixture of the reaction was filtered. For 12 hours, the precipitates were placed in an oven at 60 °C. After drying the sediment, it was placed in an oven at 80, 100, 200, and 300 degrees Celsius for one hour. Different percentages of nanocomposite films were obtained (Scheme 4).

#### 4. Conclusions

Tennis rackets made of polyamide composites reduce injuries during physical exercises because they are flexible and have a lighter structure. Compression polymerization was used to synthesize these polyamide nanocomposites with different percentages of MWCNT. A new peak at 2925  $\text{cm}^{-1}$  corresponds to the presence of MWCNT, which is evident from FTIR spectroscopy analysis of the pure polymer and its nanocomposite. TEM imaging proved that the tubes had a proper distribution and morphology. In the analysis of the synthesized polymers and nanocomposites, it was found that the thermal resistance of these polymers increased as carbon nanotubes were added in different percentages. According to TGA analysis, the high thermal conductivity of carbon nanotubes is responsible for this thermal stability. Carbon atoms were uniformly dispersed in the macromolecule matrix of NCs, as shown by SEM.

#### 5. Supporting information

##### 5.1 Experimental section

##### 5.1.1 The general method of PA/MWCNT nanocomposites synthesis

PA was synthesized by adding diamine to terephthaloyl dichloride, NMP, pyridine, and triphenyl phosphite under reflux at 110°C under nitrogen pressure for 3 hours. Finally, methanol was added to the viscous mixture and stirred for 3 hours at room temperature by a magnetic stirrer. After receiving the sediment, it was washed with hot water and dried. Polyamide was mixed with MWCNT in proportions of 5, 10, and 15%, and then DMAc was added. After stirring for 24 hours, the solvent was removed, and the precipitate was placed in a 60 °C oven for 12 hours (Shafiei *et al.* 2016c, Ghadiri *et al.* 2017, Shafiei *et al.* 2017, Azimi *et al.* 2018).

##### 5.2 Analyses of the IR spectrum, <sup>1</sup>H NMR spectrum, and C

##### 5.2.1 PA/MWCNT nanocomposites

Brown powder, M.P: 320 °C, decompose: 1479, 1508 (C=C, Ar), 1227 (C-O-C), 1375 (C-N), 2925 (C-H,

$\text{sp}^2$ stretch), 1738, 1725 (C=O amide), 1600, 3275 (N-H), 3426(O-H bond), IR (KBr) ( $\text{vmax/cm}^{-1}$ )

<sup>1</sup>H NMR,  $\delta$  (ppm): 7.3-8.2(m, 10H), 10.4, 11.6 (s, 2H) (400 MHz, DMSO-d<sub>6</sub>), Fig. 8.

##### 5.2.2 MWCNT\_COOH

IR (KBr): 3426(O-H bond), 2925 (C-H), 1635 (C=O), ( $\text{vmax/cm}^{-1}$ ).

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