

The Use of Carbon Nanotubes in Enhancing Bone Implants

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Abstract: Nowadays, traditional implants (for instance, Ti-based alloy, 316L stainless steel and Mg alloy) still suffer from defects such as poor wear resistance and may degrade and release toxic ions. These properties may inhibit cell viability, causing a stress shielding effect, and requiring multiple operations to make the implants function properly (but too many surgeries will put a burden on the patient's body). The superior mechanical properties, biocompatibility, and potential to enhance implant function have made carbon nanotubes (CNTs) a significant interest in bone implants. This study investigates the integration of CNTs into various alloys, focusing on their effects on mechanical strength, wear resistance, and biocompatibility. CNT-reinforced alloy composites exhibit enhanced tensile and compressive strengths and increased hardness, making them suitable for orthopaedic applications. In addition, CNTs improve cell adhesion and show antimicrobial properties, making them promising for reducing the infection risk of biomedical implants. CNT-doped alloys offer a lot of potential to enhance bone implant function overall, but more study is required to maximize its application in clinical situations.

Keywords: Carbon nanotubes, Bone implant, Metal implants.

1. Introduction

In recent years, the replacement of large sections of human joints or bones with artificial implants has become increasingly common, due to severe fractures, congenital deformities, bone tumours, and other conditions that cause extensive bone defects. Although bone tissue has a remarkable self-regeneration ability, in such cases, the structural and functional integrity of the regenerated bone is often difficult to restore to its original level without surgical intervention. According to Dr. Amara [1], there are currently three main clinical approaches to repairing damaged bones: autografts, allografts, and artificial implants. Autografts often face challenges related to donor site limitations and size mismatches, while allografts carry a high risk of immune rejection and complications, making them a less preferred option. As a result, artificial implants made from these traditional metals have become more widely used. However, these metal implants still face several challenges, for instance, poor resistance to wear and low biocompatibility, which necessitates the introduction of doping materials to address these issues.

In this context, carbon nanotubes (CNTs) have gradually attracted widespread attention from researchers as an emerging material. CNTs not only exhibit excellent mechanical properties (for instance, high yield strength and toughness) but also demonstrate good biocompatibility, resulting in

them being a viable candidate for biomedical applications. Studies have shown that CNTs can overcome certain drawbacks of traditional metal implants by enhancing the structural integrity of composite materials and improving bone integration capabilities [2, 3]. Additionally, surface functionalization of CNTs can enhance cell adhesion and proliferation, promoting bone tissue regeneration. Therefore, exploring the application of CNTs in bone implants not only offers new ideas for materials science but also has the potential to improve clinical treatment outcomes.

This article aims to summarise recent studies on integrating CNTs into various medical bone implants, focusing on understanding their effects on implant performance and biological compatibility. Meanwhile, the advantages and drawbacks of carbon nanotube-doped samples will be explained with actual experiments. Improvements in mechanical properties, for instance, the yield strength and resistance to wear, enhanced bioactivity as well as cellular responses facilitated by CNTs will receive specific attention. In addition, the cytotoxicity concerns and issues related to CNTs' dispersion and stability within implant materials will also be explored.

2. Mechanism & Structure of CNTs

CNTs, a type of carbon that is sp^2 - hybridized, are graphene sheets that roll into cylindrical shapes, resulting in unique hollow tube structures [4]. This structure is a foundation for its exceptional mechanical, electrical properties and biocompatibility. Due to the strong sp^2 bonds between carbon atoms, CNTs show remarkable yield strength and stiffness, far exceeding the mechanical strength of traditional alloys and metals, making them highly durable and resistant to deformation. Their superior thermal conductivity (which surpasses diamond) allows for efficient heat dissipation, while their low electrical resistance makes them excellent conductors.

The functionalization of CNTs is enabled by their large surface area and hollow structure, which allows for surface modifications that can enhance biocompatibility and cell adhesion. This makes CNTs particularly promising in biomedical applications, such as bone implants, where mechanical strength, biointegration, and longevity is critical. CNTs' ability to integrate with human tissues while resisting corrosion and degradation positions them as a valuable material for next-generation orthopaedic implants, improving both their durability and performance in clinical settings.

As Dr. Rathinavel mentioned in the article [5], carbon nanotubes could be mainly divided into three types: single-walled carbon nanotubes (SWCNT), double-walled carbon nanotubes (DWCNT), and multi-walled carbon nanotubes (MWCNT), as shown in Figure 1. The SWCNTs can be synthesized using arc-discharge and laser-ablation techniques [4]. These methods need the presence of metal catalysts, typically nickel (Ni) or cobalt (Co), to regulate the diameter of the SWCNTs in the wanted region. The growth process is generally carried out at high temperatures, ranging from 2000 to 3000 K. MWCNTs, including DWCNTs, can be viewed as a series of concentric SWCNTs with varying diameters. Due to space limitations, not all diameters can fit perfectly inside one another, making it essential to maintain a gap of approximately 3.44 Å between each tube layer [5]. The Russian Doll model, in which the carbon nanotubes are nestled within one another, and the Parchment model, in which a single graphene sheet is wrapped into several layers, are the two structural forms that MWCNTs can form.

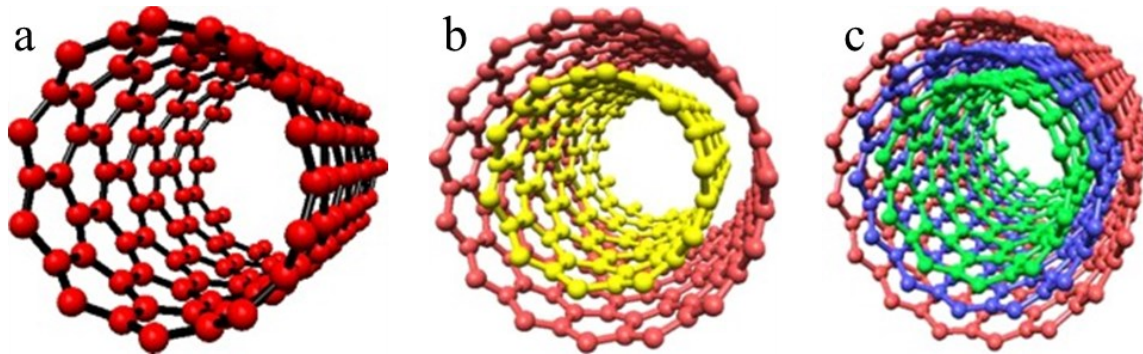


Figure 1: Three types of CNTs: SWCNT (left), DWCNT (middle), MWCNT (right) [5]

3. The introduction of carbon nanotubes in bone implants

3.1. Carbon nanotubes doped Mg alloy:

CNTs are well-suited for biomedical implants due to their exceptional mechanical strength, thermal conductivity, and electrical properties. Their properties for instance good biocompatibility and tissue integration, give the CNTs a significant advantage over traditional materials used in medical implants. These unique properties make CNTs a considerable material in doping with other materials to build a fitting implant.

The tensile strength and Young's modulus of several materials are displayed in Figure 2 below. It is evident that magnesium has a similar mechanical characteristic with human bone. As previously mentioned, due to titanium alloys and cobalt-chromium alloys are significantly stiffer than human bone, it can lead to bone loss due to the stress shielding effect [6]. Furthermore, Dr. Wang [7] pointed out that prolonged implantation of bioinert metallic implants can cause the drilled site to become stuck, making revision procedures more difficult. In contrast, Dr. Wang highlights that degradable magnesium-based alloys, which possess higher strength but has a Young's modulus which is close to that of human bone, are well-suited for implants. These characteristics make them a better choice for lowering long-term issues by minimizing the stress shielding effect during load transmission at the implant-bone interface.

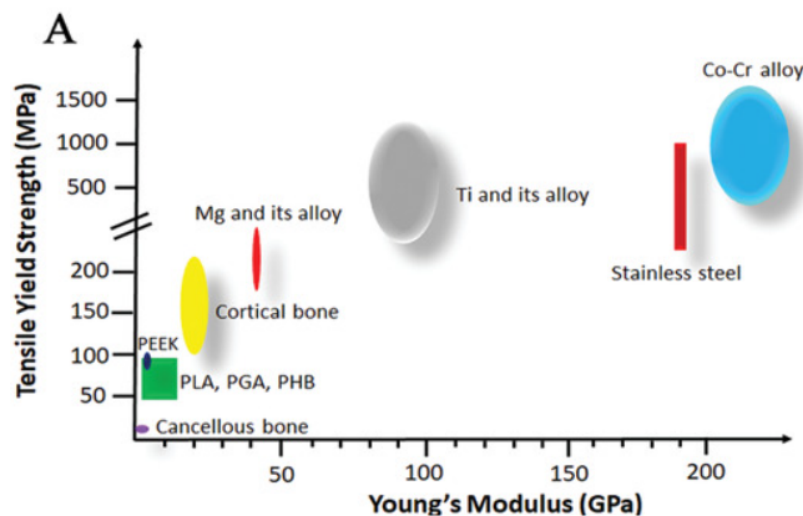


Figure 2: The range of tensile yield strength and Young's modulus of materials include natural bone, and alloys which are used in the medical implants nowadays; [7]

While degradable magnesium (Mg) implants may release excess Mg ions into the body, this does not pose a health risk, as the ions can be safely excreted through normal metabolic processes. However, controlling the degradation rate of Mg remains a challenge, as cavities surrounded by fibrous tissue near the implant site may form as a result of rapid degradation, potentially causing inflammatory responses. Additionally, the mechanical strength of Mg is not always sufficient, and there have been cases where screw heads broke during surgery due to the material's fragility [7].

Dr. Abazari's research highlights that in order to overcome the defects (high degradation rate, low mechanical strength, and poor to-wear resistance) of doping magnesium-zinc composite (Mg-3Zn) fibrous carbon nanotubes (fCNTs) could be introduced to form the Mg-3Zn/x fCNTs ($x = 0, 0.2, 0.4$, and 0.8 wt%), and it will greatly enhance the material's mechanical properties, corrosion resistance, and biocompatibility. Figure 3a shows that incorporating fCNTs into the matrix enhances the composite's microhardness, with higher fCNT concentrations leading to further increases in microhardness. Figure 3b presents the compression strength, another crucial factor for bone implants. The Mg-3Zn composites doped with 0.2%, 0.4%, and 0.8% fCNTs showed compression strengths of 368.2, 390, and 320.2 MPa, respectively, along with microhardness values of 70, 74, and 76 HV, compared to the pure Mg-3Zn alloy (289.6 MPa and 66 HV). Notably, at 0.4% fCNTs, the compression strength maximized. Mg-3Zn reinforced with fCNTs is often stiffer than Mg-3Zn composites, according to ultimate compressive strength (UCS) and strain to failure (Fig. 4a, Table 1). From these results, fCNTs are proven to considerably improve the mechanical performance of Mg-3Zn alloys, giving human bone enough mechanical support to tolerate flexural pressure upon implantation [8].

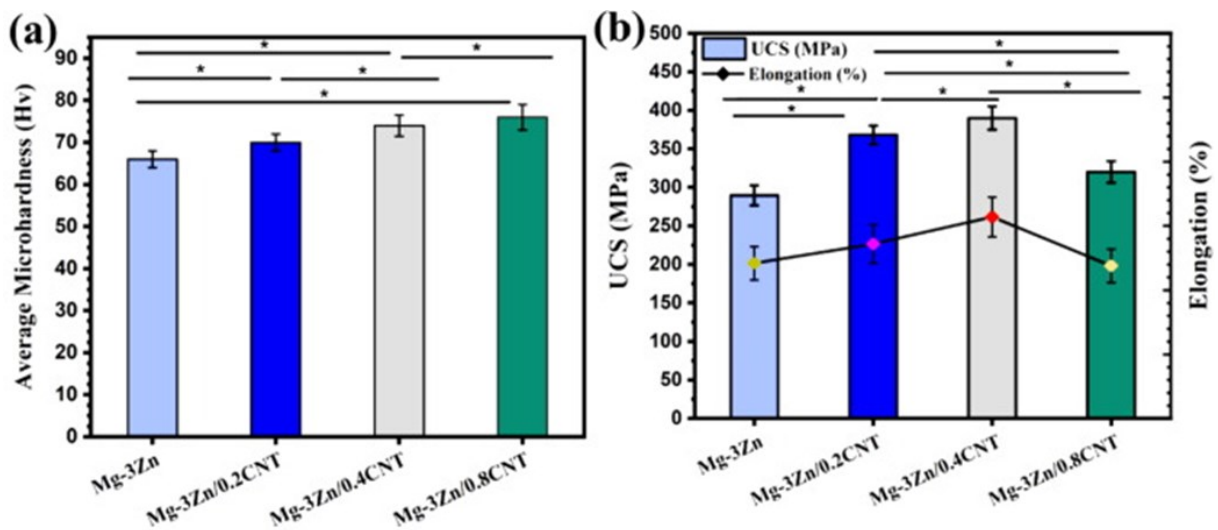


Figure 3: (a) Microhardness of composites doped with different concentration of CNTs, (b) Values of UCS and failure strain of composites doped with different concentration of CNTs [8]

Table 1 [8] showcases the fundamental physical characteristics of Mg-based composites reinforced with fCNTs, which include UCS, failure strain, and hardness. The results show that incorporating small amounts of fCNTs (0.2-0.8 wt%) significantly enhances the mechanical performance, particularly by improving bending and tensile strength through a crack-bridging effect, which is visible in the Figure 5 below:

Table 1: Comparison of mechanical properties of Mg alloy doped with CNTs, with Alloys without the doping of fCNTs. (SPM: Semi powder metallurgy, E: Elastic modulus.) [8]

Sample	Fabrication Method	E (Gpa)	UCS (Mpa)	Failure Strain (%)	Hardness (HV)
Mg-3Zn	SPM followed by hot extrusion	15.06±2.5	289.6±13	12.1±1.3	66±2
Mg-3Zn/0.2fCNTs	SPM followed by hot extrusion	28.47±1.3	368.2±12	13.6±1.5	70±2
Mg-3Zn/0.4fCNTs	SPM followed by hot extrusion	27.32±2.3	390±15	15.7±1.5	74±2.5
Mg-3Zn/0.8fCNTs	SPM followed by hot extrusion	21.94±1.4	320.2±14	11.9±1.3	76±3

Figure 4b and 4c shows 2 different crack propagation mechanism which contributes to fail of implants, while 4a) and d) shows the effect of CNTs in stoping the crack on the surface of the alloy from propagating. In summary, the Mg-3Zn/0.4fCNTs composite had the highest compressive strength (390 ± 15 MPa), surpassing cortical bone (164–240 MPa) and other Mg-based composites like Mg-3Zn/15HA (257.3 ± 5.4 MPa), Mg-3Zn-5HA (134 ± 3 MPa), Mg-3Zn-0.5Ag (190.9 MPa), and Mg-2.5TiO₂ (305.5 ± 11 MPa). Dr. Abazari [8] states that to guarantee a 90–180-day service life, biodegradable orthopedic implants should have a strength excess 200 MPa and at least an 10% elongation. This threshold is exceeded by the Mg-3Zn/0.4fCNTs composite, indicating its potential for long-term application in biodegradable orthopedic implants.

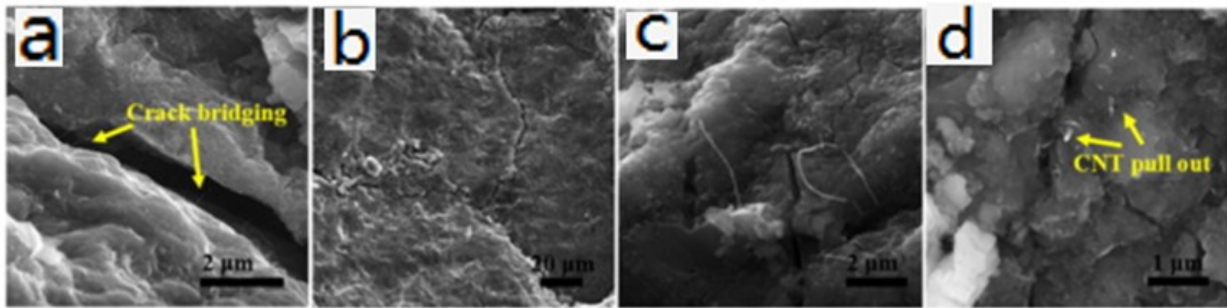


Figure 4: Images of (a) crack bridging, (b) fCNTs pull out. [8]

It has been discovered that the hydrophilicity of scaffolds had a favourable effect on both protein adsorption and cell adhesion because successful implant integration depends on tissue attachment, which starts with cell adhesion to the implant surface and progresses to protein adsorption that encourages cell binding and biological reactions [9]. Figure 5a exhibits Dr. Abazari's experimental findings that indicate that the water contact angle decreases as the concentration of CNTs in the alloy increases, which indicates an increase in hydrophilicity. According to Dr. Maghimaa [10], a higher CNT concentration (0.8%) should theoretically promote greater cell attachment than 0.4%. However, Figure 5b shows a significant decrease in the number of cells attached to the implant surface when the CNT concentration rises to 0.8%. Additionally, as shown in Figure 5c, the osteoblasts on the Mg-3Zn/0.4fCNTs composite exhibit a more rounded morphology. These findings suggest that while increasing CNT content can improve hydrophilicity and cell adhesion, excessively high concentrations may negatively affect osteoblast attachment, cells spreading, and their proliferation.

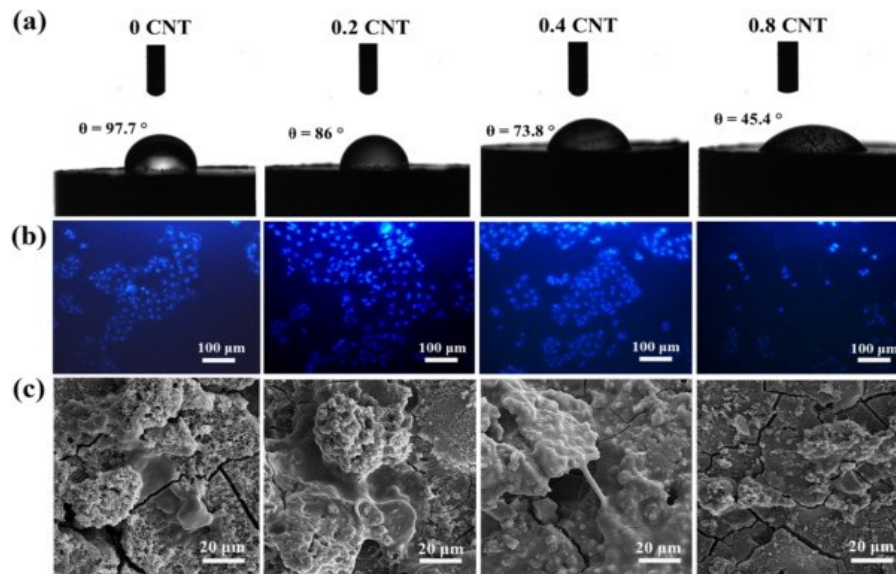


Figure 5: The images of cells attachment for different proportion of CNTs after 3 days of cultivation; a) Images of water contact angle, (b) Fluorescent DAPI staining of MG-63 cells grown after 24 h, and (c) SEM images of the morphology and adhesion. [8]

Cell viability of fibroblast-like human osteosarcoma cells (MG-63 cells) on materials with different CNT concentrations is shown in Figure 6. The cell viability for Mg-3Zn, Mg-3Zn/0.2fCNTs, Mg-3Zn/0.4fCNTs, and Mg-3Zn/0.8fCNTs was 90%, 95%, 98%, and 86%, respectively, following three days of incubation, as shown in Figure 6a and 6b. These results align with the findings from Figure 5, indicating that while CNTs enhance cell viability up to a certain concentration, beyond 0.8 wt%, they no longer promote cell attachment and may even reduce viability. Nevertheless, the viability remains well above the 75% threshold for good cytocompatibility [11].

Dr. Abazari [8] attributes this effect to the increased hydrophilicity caused by higher CNT concentrations. At elevated CNT levels in the Mg-3Zn alloy matrix, CNTs tend to aggregate, creating more hydrophilic surfaces. This, in turn, can lead to galvanic and crevice corrosion in simulated body fluid (SBF), reducing the composite's corrosion resistance. As a result, more Mg ions are released into the body compared to Mg-3Zn alloys without CNTs, and it is found that the release of excess Mg ions will inhibit cell viability [12].

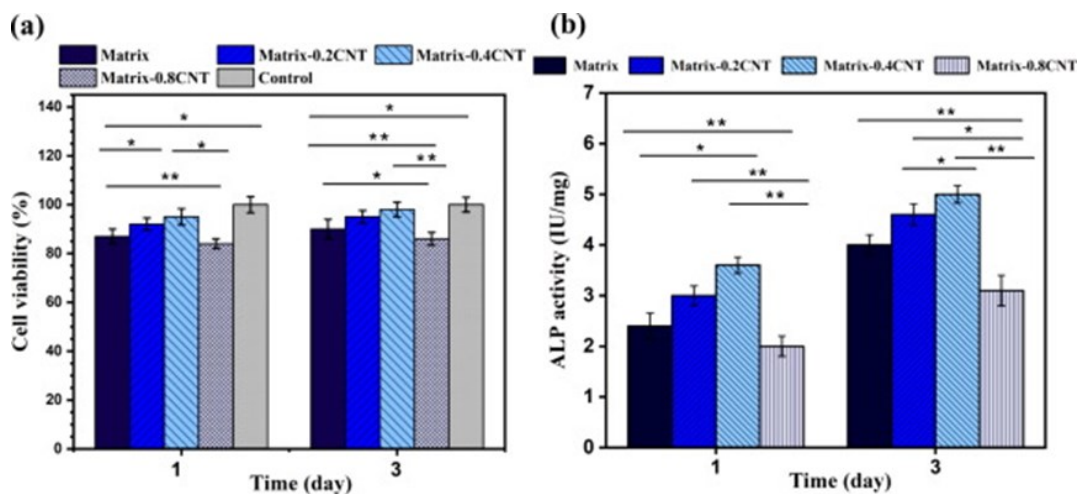


Figure 6: (a) cell viability and (b) ALP activity of MG-63 cells observed after 1 day and 3 days on Mg-3Zn/xfCNTs nanocomposites [8].

3.2. The introduction of carbon nanotubes in Ti bone implants

As previously mentioned, Ti-based alloys are one of the most widely utilized materials for bone implants because of their exceptional mechanical properties and good biocompatibility. Despite their advantages, they do have some drawbacks, such as a discrepancy in Young's modulus and tensile yield strength when compared to human bone. Figure 3 illustrates the significant disparity in Young's modulus and tensile yield strength between human bone and the alloys typically found in implants today, which can lead to the stress shielding effect, weakening the surrounding bone. Additionally, their low wear resistance [13] can result in implant failure over time, potentially requiring a second surgery.

According to Dr. Munir [14], the TNZ composite reinforced with multi-walled carbon nanotubes (TNZCNT) has better mechanical properties than the new β Ti-28Nb-35.4Zr alloy (TNZ). Following the DMD procedure, a compression test was performed on the TNZ and TNZCNT samples in Dr. Munir's work. Both TNZ and TNZCNT exhibit a great capacity for plastic deformation without developing fractures or fissures. When the compression force hit 48 kN, the test was terminated. Table 2 provides the following summary of the resulting mechanical properties:

Table 2: Comparison of several properties of Ti-based alloys and composite (σ_{CYS} = compressive yield strength; E = elastic modulus; H_n = nano-hardness; H_m = microhardness.). [14]

Composition	Method	σ_{CYS} (Gpa)	E (Gpa)	H_n (GPa)	Wear volume (μm^3)	H_m (HV)
TNZ	DMD	706 $\pm$ 16	69.0 $\pm$ 1.6	2.9 $\pm$ 0.1	0.19 $\pm$ 0.04	250 $\pm$ 4
TNZCNT	-	833 $\pm$ 4	80.0 $\pm$ 3.1	3.4 $\pm$ 0.5	0.07 $\pm$ 0.05	270 $\pm$ 8
TNZ	SLM	768 $\pm$ 30	60.0 $\pm$ 2.0	—	—	—
TNZ	Casting	741 $\pm$ 15	71.0 $\pm$ 1.5	1.8 $\pm$ 0.1	0.25 $\pm$ 0.03	244 $\pm$ 2
TiNbZr0.2Ti	Arc melting	740	74.5	—	—	235 $\pm$ 7

TNZCNT demonstrated a nanohardness of 3.4 GPa, as opposed to 2.9 GPa for TNZ, and a compressive yield strength of 833 MPa, as opposed to 706 MPa for TNZ. Furthermore, because of its higher hardness, TNZCNT showed improved resistance to wear. In contrast, TNZCNT's nanohardness and elastic modulus are 17% and 16% higher than those of TNZ. MWCNTs provide a beneficial contribution to the hardness of bone implants, as evidenced by the TNZCNT composite's average Vickers hardness of 270HV, which was 8% greater than that of TNZ [14].

Apart from that, the CNTs doped samples shows better biocompatibility, as shown in the Figure 7 below. This Figure 7 shows the viability of SaOS₂ cells after 1 day and 7 days on different materials. The cells in the environment of TNZCNT material shows a higher viability after both day 1 and day 7. This is a result of TNZCNT materials' reduced grain sizes following carbon nanotube doping, which also increases the number of bioactivity sites and encourages cell adhesion and proliferation [14]. Meanwhile, by generating a permeant charge on the implant surface, MWCNTs may improve cell adhesion and differentiation, according to Dr. Zhao [15]. As a result, MWCNTs and cell-binding proteins will interact.

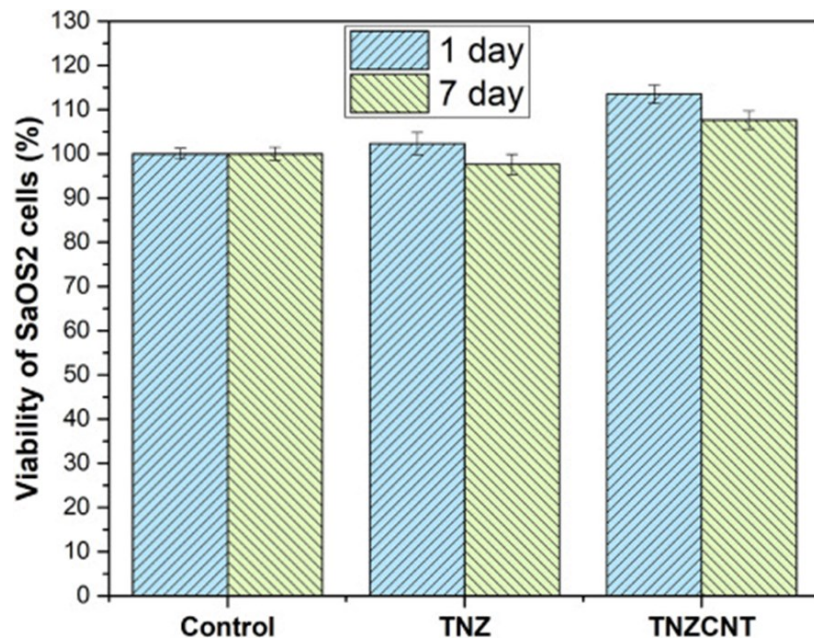


Figure 7: DMD-processed TNZ composites' in vitro cytotoxicity in osteoblast-like SaOS2 cells following one and seven days of cell culture [14].

3.3. The introduction of carbon nanotubes in 316L Stainless Steel

The low corrosion resistance of 316L stainless steel implants is one of their biggest disadvantages. In human body environment the Stainless Steel will corrode rapidly and release Ni ions which has been prove to be highly toxic to health. Dr. Bowden claims that when CNTs are used to modify the surface of 316L stainless steel, it will lose its passivating layer and undergo oxidative corrosion in an aqueous environment [16], or in other words, the human body. Undoubtfully, this process will lead to faster corrosion rate of 316L Stainless Steel, and it led to limit use of carbon nanotubes in doping with 316L Stainless Steel.

4. Conclusion

The features of carbon nanotubes and their potential to improve various bone implant alloys are highlighted in this article. When CNTs are added to the alloy matrix, mechanical qualities, corrosion resistance, and biocompatibility all significantly improve. For instance, the reinforced Mg-3Zn alloy exhibited higher tensile strength and hardness, making it an ideal orthopaedic implant. In the meanwhile, doping CNTs into alloys may match the mechanical characteristics of CNRs and lessen the likelihood that a stress shielding effect will emerge, which causes bone loss. In the meantime, the CNTs' inherent antibacterial qualities and their function in enhancing osteoblast adhesion highlight their potential to lower infection risks and encourage tissue integration.

However, challenges still exist. The high proportion of CNTs in the metal implants will lead to more hydrophilic surfaces and therefore induce excessive degradation and cytotoxicity remains. CNT-doped alloys are a promising avenue for future orthopaedic materials. Further research is necessary to fine-tune the balance between their mechanical enhancements and potential biocompatibility concerns

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