Journal of Science: Advanced Materials and Devices 8 (2023) 100557

Contents lists available at ScienceDirect

Journal of Science: Advanced Materials and Devices

journal homepage: www.elsevier.com/locate/jsamd

Review Article

# Carbon nanotube-reinforced polymer nanocomposites for sustainable biomedical applications: A review

Oladiran Kamardeen Abubakre [a], Rasaq Olawale Medupin [b], Idris Babatunde Akintunde [a], Oladejo Tijani Jimoh [c], Ambali Saka Abdulkareem [d], Rasheed Aremu Muriana [a], John Adeniran James [e], Kingsley O. Ukoba [f], Tien-Chien Jen [f], Kelvin O. Yoro [g, *]

[a] *Department of Materials and Metallurgical Engineering, Federal University of Technology, P.M.B. 65, Minna, Nigeria*
[b] *Department of Materials and Metallurgical Engineering, Federal University of Technology, P.M.B. 1526, Owerri, Nigeria*
[c] *Department of Chemistry, Federal University of Technology, P.M.B. 65, Minna, Nigeria*
[d] *Department of Chemical Engineering, Federal University of Technology, P.M.B. 65, Minna, Nigeria*
[e] *Department of Surgery, Federal Medical Centre, P.M.B. 14, Bida, Nigeria*
[f] *Department of Mechanical Engineering Science, University of Johannesburg, Auckland Park Campus, Auckland Park, 2092, Johannesburg, South Africa*
[g] *Energy Technologies Area, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA, 94720, United States*

## ARTICLE INFO

*Article history:*
Received 24 September 2022
Received in revised form
6 March 2023
Accepted 18 March 2023
Available online 24 March 2023

*Keywords:*
Carbon nanotube
Natural rubber
Polymer nanocomposites
Prosthetics
Biomedical application

## ABSTRACT

The search for viable alternatives to conventional materials in biomedical applications is as important as the movement for the adoption of a sustainability approach in the production of polymer nanocomposites for prosthetic purposes. Carbon nanotube (CNT) reinforced polymer nanocomposites have become the center of the present prosthetic industry due to their unparalleled strength-to-weight characteristics. However, the categories of polymers used for this purpose and their long-term impact on the environment have generated controversies among researchers. The adequacy, affordability, and sustainability of materials for the development of prosthetics are some of the common concerns. Consequently, this review addresses concerns about the adherence to SDGs in biomedical manufacturing which focuses on material selection considering environmental impacts. In addition, contributions from previous research were reviewed based on the remarkable increase in the number of publications on CNT-reinforced polymer nanocomposites over the last 10 years. Various findings by researchers in the field who used natural rubber and other polymers as host matrices were analyzed from the perspective of sustainability. While considerable progress has been made in the use of other polymers in the biomedical field, only a few publications have targeted natural rubber. This review provides insights into opportunities for sustainable production and consumption of devices with biodegradable CNT/natural rubber nanocomposites.

## 1. Introduction

The role of carbon nanotubes (CNTs) in the current and future development of materials science and technology has been extensively studied [1,2]. Although its importance might not be fully appreciated in its pristine form, the significant impact it has on the overall properties of other bulk materials where it serves as filler or adjoining ancillary part have shown that there is more to the application of CNTs than is currently known and/or reported [3]. Despite being concerned about the need for atomically developed entities to be useful to humans, the real challenge of incorporating nanomaterials such as CNTs, into host materials such as polymers and metallic materials for various applications has sparked interest in CNT research globally. There have been reports of CNTs being used as reinforcing fillers in polymers, ceramics, and metals for different applications revealing enhanced tensile strength, hardness, and elastic modulus characteristics of the materials [4]. The application of this technology in medicine and biomedical engineering encompasses areas such as diagnosis and therapy, tissue

---

* Corresponding author.
*E-mail addresses:* diranabubakre@futminna.edu.ng (O.K. Abubakre), medupinwale@gmail.com (R.O. Medupin), i.akintunde@futminna.edu.ng (I.B. Akintunde), jimohtijani@futminna.edu.ng (O.T. Jimoh), kasaka2003@futminna.edu.ng (A.S. Abdulkareem), mraremu@futminna.edu.ng (R.A. Muriana), jayjaytonaniran@yahoo.com (J.A. James), ukobaking@yahoo.com (K.O. Ukoba), tcjen@uj.ac.za (T.-C. Jen), kelvin.yoroo@gmail.com (K.O. Yoro).

Peer review under responsibility of Vietnam National University, Hanoi.

https://doi.org/10.1016/j.jsamd.2023.100557

engineering [5,6], and, more recently, prostheses and orthotics [7–9], among others.

The structure of CNTs is formed by a layer of carbon atoms bonded together in a hexagonal mesh. While the structure of single-walled carbon nanotubes (SWCNT) can be pictured as a rolled-up tubular shell of a graphene sheet which is made up of benzene-type hexagonal rings of carbon atoms, multi-walled carbon nanotubes (MWCNT) is a stack of graphene sheets rolled up into concentric cylinders as a combination of several SWCNTs. According to Siafuddin et al. [10], CNTs are different from carbon fibers, which are not single molecules but strands of layered-graphite sheets. They are said to have a higher tensile strength than steel and Kevlar as a result of the $sp^2$ bonds between the individual carbon atoms and can be made even stronger than the $sp^3$ bond found in diamonds. CNTs are also available in coated, dispersed, and functionalized forms to be preferentially adsorbed at the surface interface using chemically bound polymers. Like other earlier reports, Takakura et al. [11] observed that the strength of CNTs depends on the chiral structure of the nanotube, with small-diameter, near-armchair nanotubes exhibiting the highest tensile strengths. This observed structural dependence is understood via the intrinsic structure-dependent inter-atomic stress, with its concentration at structural defects unavoidably present in nanotubes. This highlights the structures of CNTs necessary to fabricate the strongest composites [11].

CNT-reinforced polymer nanocomposites have extensive application prospects in many fields of science and engineering owing to their exceptional properties such as lightweight, high specific strength, high aspect ratio, and high specific stiffness [12–14]. Since the discovery by Iijima in 1991, the interests of many polymers composite experts have been aroused as they seek ways to harness the enormous strength of CNTs to plug the gaps associated with natural fiber-reinforced polymer nanocomposites with synthetic filler which has demonstrated superior mechanical strength [15]. The preference for natural fillers has always been linked to their easy availability, ecological friendliness, and earlier biodegradability when compared to their synthetic counterparts [16–18]. However, these biases can be traded off for strength and long fatigue life in some critical applications where safety supersedes other considerations [19]. Players in the polymer composite field have worked with different polymer materials, ranging from thermoplastics to elastomers using both natural and synthetic filler materials with varying degrees of success [5,7,8,14–16,19–24]. Synthetic fillers used as reinforcing agents in host polymers include silicon carbide (SiC), aluminum oxide ($Al_2O_3$), zinc oxide (ZnO), graphite, zeolite, calcium carbonate ($CaCO_3$), magnesium hydroxide ($Mg(OH)_2$), boron carbide ($B_4C$) and carbon powder. Others include silicon dioxide ($SiO_2$), titanium dioxide ($TiO_2$), zirconium dioxide ($ZrO_2$), and tungsten carbide (WC) [25]. Some of the popular natural filler agents include, among others, jute, sisal, hemp, bamboo fibers, grass fibers, and bagasse [51].

Several definitions have been adopted for the description of natural and synthetic fibers as used in polymer science and engineering. The definitions are tailored toward the applications of the resulting composites and generally pivoted on climate change compliance. Despite numerous advantages of synthetic fibers as a reinforcing agent, rising environmental concerns around manufacturing costs, disposal, as a result of non-biodegradability, and reuse favor the quest for alternative materials in natural fiber for eco-friendly and biodegradable composite in other applications [16,17,19,26,27]. Therefore, to find a balance between the high mechanical properties of synthetic fibers and the eco-friendly nature of renewable fibers, scientists have reinforced polymer matrices with hybrid fibers (natural and synthetic) for highly specific and determined properties [28]. Despite such exceptional properties exhibited by CNTs and an array of prospective areas of applications, their innate color appears to limit their usage in certain areas. While a chemically pure and structurally perfect $sp^3$-bonded diamond is colorless (transparent), $sp^2$-bonded graphitic structures, including CNTs, usually appear black [29]. This somewhat puts off prospective users where the intrinsic strength of the material is to be leveraged to reinforce polymer materials for anthropomorphic prosthetic limb application (meant to not only mimic the anatomical parts but also hide the disability). Therefore, given the growing appreciation of CNTs as one of the most sought-after fillers in polymer matrices and the increasing demand for less expensive prosthetics for the growing population of amputees in low-income countries, a clear understanding of the past, present, and future of CNTs reinforced natural rubber is necessary. Moreover, literature on CNTs-reinforced polymer matrices with a particular focus on natural rubber is limited. The few available hardly explore the biomedical prospects of the materials.

Given the epidemiological nature of below-knee amputation and the widespread concerns regarding the restoration of quality of life for amputees [30], hundreds of thousands of prosthetics find their way into low-income countries yearly. And as a result, it becomes difficult to provide a regulatory framework for the influx of both standard and sub-standard prostheses into the countries because players in the prosthetic industry are often more concerned about satisfying the shareholders of their business than they are of the stakeholders (prosthetics customer and users) who are the drivers of the industry. Furthermore, other salient questions about the suitability, affordability, and sustainability of materials for prosthetic development are raised. Consequent to this, we propose the use of a triple bottom line (TBL) conceptual framework to address the burning concerns around adherence to the UN's sustainable development goals in the manufacture of prosthetic devices while maximizing profits but not at the expense of the environment. The TBL, which was originally designed to solve concerns/challenges in the way businesses are run has proven to not only be applicable in the business world, but also in all areas of human activities, including waste management [31], measurements [32] and, of course, manufacturing [33]. It is a methodology that thrives on the principle of sustainability; established on the tripod of economy, environment, and society. It suggests, therefore, that both social and environmental impacts should be accorded equal attention to the financial performance of any organization. At the core of the concept is sustainability as advocated in the SDGs. This review explores polymer matrix composites to foster a wave of changes to the CNT/NR project nanocomposites as potential candidates for biomedical devices under the United Nations Sustainable Development Goals 12 for Sustainable Production and Consumption.

While several review articles have been published in many areas of rubber nanocomposites; with most of them focused on synthetic rather than natural rubber (NR), only a few directly addressed the applicability of NR/CNTs nanocomposites for in-vitro biomedical purposes. Thus, this study identifies, synthesizes, and interprets existing literature on the development of CNTs/polymer nanocomposites for biomedical applications. It crisscrosses the manufacturing procedure for rubber nanocomposites, CNTs-reinforced nanocomposites, properties of polymer nanocomposites; brief reviews of current trends in CNTs/NR nanocomposites and closes with a strong advocacy for sustainability in the development of CNTs/NR nanocomposites which is rare in the literature.

## 2. Polymer nanocomposites fabrication procedure

The need to reinforce polymeric matrices for load-bearing purposes has become popular among researchers over the years.

However, the complexities associated with its fabrication process constitutes a major limitation. Fig. 1 describes a typical process for fabricating CNTs-reinforced polymer nanocomposites (elastomers in this case). It illustrates the general procedure for fabricating carbon nanofillers-reinforced polymer composites. After the purification and sonication processes were completed, the fillers were introduced into the host matrix and stirred mechanically, after which it was cured under a controlled atmosphere. Any chosen manufacturing technique could, then, be employed for the manufacture of the bulk product (casting was adopted in Fig. 1). Some of the chemicals used for the synthesis of CNTs eventually find their way into the mainstream CNTs as impurities; prompting the need to remove them to harness the full potentials of the materials; hence CNT purification. CNTs' purification can be described as the process of separating nanotubes from non-nanotube inclusions [34] and the removal of nanotubes of undesirable geometry [34]. The whole essence of purification stems from the desire to remove amorphous carbon to improve the surface area and decompose functional groups thereby blocking pore openings to make way for easy interfacial interaction between filler and matrix phases. An approach consistent with the selective oxidation of carbonaceous impurities by heating at a gradually rising temperature in air was described by Berrada et al. [35]. While Jahanshahi & Kiadehi [34] reported less damage to the structure of CNTs (Fig. 2: different allotropes of CNTs used in various applications) during purification, other researchers opined that no matter what method is used, destruction of CNTs' structure is always almost unavoidable. However, to take care of oxidizing metallic impurities incorporated during synthesis, oxidation remains the preferred method.

Oxidative purification, which could be carried out either in the liquid or gaseous phase, has been widely used for the purification of synthesized CNTs due to its relative simplicity, cost-effectiveness, and scalability [36–38]. Solutions of concentrated acids like HCl, $HNO_3$, and $H_2SO_4$ or strong oxidants are generally used in the liquid phase oxidation while the gas phase employs air, oxygen, or other gases at controlled temperatures. The approach takes advantage of a selective oxidative etching process, based on the premise that amorphous carbon and carbon particles can be more easily eliminated due to their higher oxidation reaction rate than CNTs [39]. According to Ismail et al. [36], the high oxidative activity demonstrated by the amorphous carbon is largely attributed to the presence of hanging bonds with high energy, which oxidizes easily. While liquid phase oxidation techniques have been proven to successfully purify and enhance the performance of CNT fibers, it has been reported to be capable of causing surface chemical modification, diameter reduction as well as possible fragmentation of the CNTs which are not good signals for some industrial applications [39]. It may also result in tips' opening of the nanotubes thereby making them susceptible to oxidative reactions alongside the amorphous particles as a result of attacks on the defective sites on the CNTs themselves. Therefore, careful design and optimization of the oxidative treatment are necessary to balance impurity removal requirements, CNT structure preservation, and improved performance of CNT fibers because gas phase oxidation has not been proven to be a more effective method.

Air oxidation is the most popular of the gas phase oxidation of CNTs. At moderate temperatures, this method can be effective in removing amorphous carbon and other carbonaceous particles. However, the presence of oxygen could damage CNTs walls and

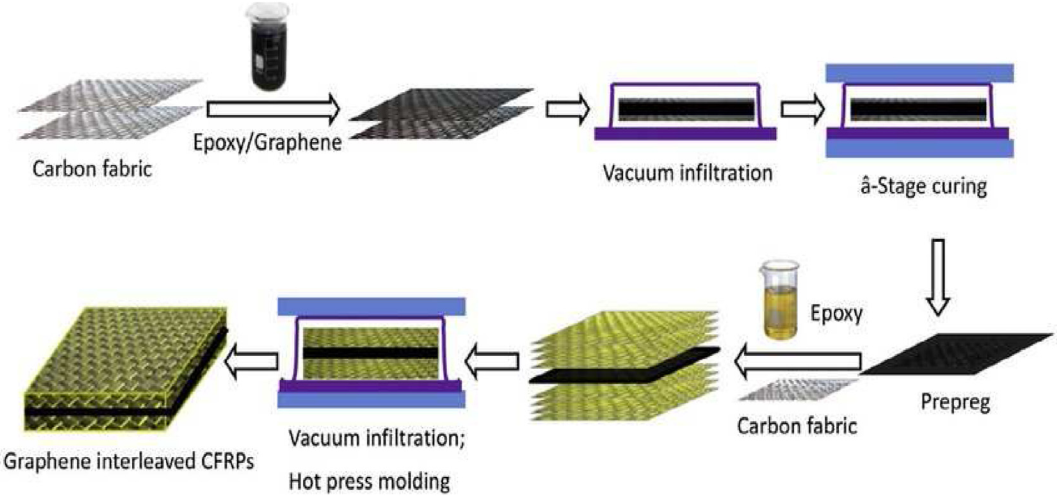

**Fig. 1.** Schematic illustration of surfactant interaction with carbon nanofiller during reinforced polymer nanocomposites fabrication [40]. Adapted with permission from Elsevier.

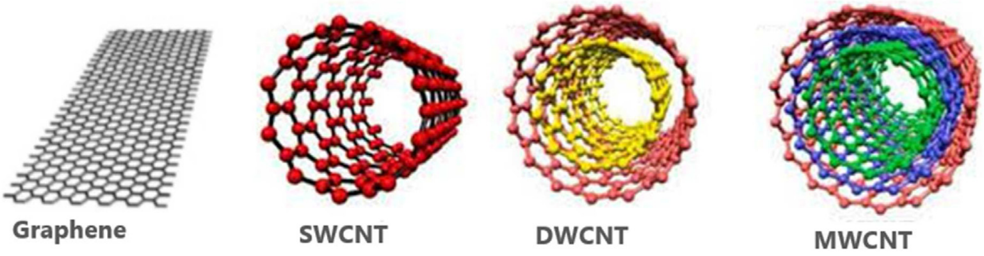

**Fig. 2.** Nano-allotropes of carbon: (a) graphene sheet (b) SWCNT (c) DWCNT (d) MWCNT [41].

weaken the strong van der Waals forces that bind individual CNTs together [37,39]. Researchers who have used this method to purify CNTs always deployed selective oxidation as up to 90% of CNTs could be lost and the structure severely damaged in the process. It is against this background that the method may not appeal to researchers who may be interested in the uniformity of the wall diameter for application in electronic devices requiring short undamaged CNTs of specific band gaps and precise length in a specific location. Moreover, the discrete nature of the process means that high activation energy is required for diameter-selective purification. Different from liquid phase oxidation, gas phase oxidation specially oxidizes CNTs without causing damage to their sidewalls [37]. In addition, a very simple apparatus is needed in gas phase oxidation and post-purification separation is unnecessary. Therefore, depending on the area of applications and other considerations, either liquid or gas-phase oxidation can be employed. However, liquid purification enjoys more patronage in recent times.

Interestingly, an aspect of the fabrication of polymer nanocomposites that has attracted the interest of researchers over the years is the dispersion of the purified nanofillers in the polymer matrix [42]. Disentanglement of nano-agglomerates and their uniform distribution throughout the matrix (as the strength of CNTs lies in the ability to make them exist as single entities [43]; breaking the intermolecular interactions amongst them) is the objective of the process. In another study, it was reported that remaining uniformly dispersed in the matrix after the processing is as important as the dispersion itself, hence, the need to functionalize the purified CNTs [44]. Ultrasonication is widely used to induce the separation of CNTs nano-agglomerates with high-frequency sound waves. This works by the principle of inertial cavitation with quick development and rapid breakdown of voids in the liquid, producing forceful shear forces. This is achieved in the presence of surfactants like sodium dodecylbenzene sulfonate with the high-speed homogenizer [7].

Berrada et al. [35] reported some transition metal-based impurities which got into the CNTs through the catalyst used for the synthesis. The latter implies about 10% of the sample weight. There are also metallic impurities amounting to 30% of the sample weight. Fig. 3 typifies the characteristic behavior of CNT samples post-$Cl_2$ and $Cl_2/O_2$ treatments [35]. The thermogravimetric analysis (TGA) profiles and combustion temperatures for double-wall carbon nanotubes (DWCNTs) samples are comparable (approximately 500 °C) before and after purification (Fig. 3(a)). Raw single-wall CNTs, however, reportedly got burned off around 350 °C; about 50 °C higher than that of DWCNTs after purification (Fig. 3(b)).

Covalent and non-covalent functionalization are generally deployed to chemically disperse CNTs in polymer hosts. CNTs walls tend to open to more functional groups while non-covalent directly grafts the functional groups on the exterior walls during functionalization. The identified challenges associated with dispersibility and nano-agglomerates of CNTs are solved with the opening of new functional groups [45]. However, two main disadvantages of covalent functionalization were identified by Syrgiannis et al. [46] as defective side walls and, therefore, inevitable disintegration of CNT in some extreme cases. These significantly damage the quality of CNTs, dismantle the π-electron system and produce defective sites. The electrons and phonons that disperse the thermal conductivity and electrical conductivity of the CNT are responsible for each of the thermal conductivity and electrical conductivity of the CNTs [47]. Secondly, the use of concentrated acids and powerful oxidants is harmful to the environment and infringes on the United Nations Sustainable Development call. Therefore, efforts are being intensified to develop affordable and convenient techniques that are less damaging to the structure of the CNTs and the environment. The result of this proposition is keenly awaited to mitigate the CNT dispersion problem permanently. However, to mitigate the pitfalls already identified, the combination of mechanical and chemical methods of dispersion is usually adopted [7].

## 3. Natural and synthetic fiber-reinforced polymer composites for biomedical application

A greater percentage of the literature on fiber-reinforced polymer composites is centered on thermoplastics rather than elastomers and natural rubber matrices for natural and synthetic filler reinforcement [48]. Global market reports on the Compound Annual Growth Rate (CAGR) for different categories justify the trend (CAGR of 9.2% for natural fiber-reinforced composite and 5% for synthetic fiber-reinforced polymer composite (FRPC) by 2023). The advantages of the natural fiber reinforced polymer market over its synthetic counterpart in terms of biodegradability, renewability (primarily from plants, animals, and regenerated sources), and low cost of the materials could be responsible for this market differentials. Kappenthuler & Seeger [48] assessed the long-term potential of FRPCs for sustainable marine construction. Despite the benefit accruable from the use of the materials, the authors expressed concerns about the liability of synthetic-based FRPCs to conditions in the marine environment vis-à-vis the effects of their economic and environmental sustainability performance. Capturing economic, environmental, and resource perspectives in a

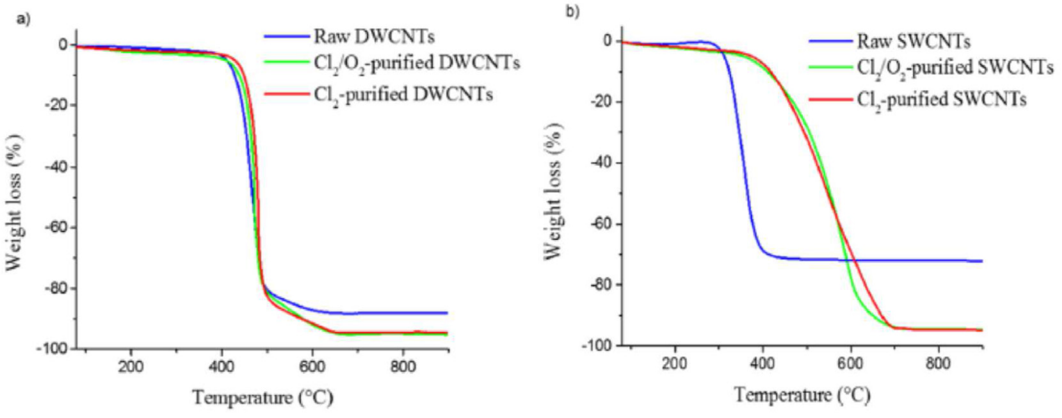

**Fig. 3.** TGA curves for the raw and selected CNTs treated with $Cl_2$ and $Cl_2/O_2$ [35].

holistic comparison of the performance of different FRPCs, they concluded that carbon fiber ranked highest ahead of basalt and glass fiber composites in mechanical and chemical resistance performance for marine applications. Like earlier researchers, Kappenthuler & Seeger [48] never gave a thought to natural fiber in the extreme conditions present in the marine space regardless of their lower cost, eco-friendlier alternatives [49] because of issues around mechanical strength and high biodegradability rate. Kumar et al. [50], in a review, examined the influence of loading and geometrical length of leaf-extracted fibers on the physicomechanical properties of different matrices-based composites while highlighting the effect of surface modifications on fiber/matrix adhesion. They observed that the reservations expressed about synthetic and other natural fibers are naturally addressed with natural leaf fibers treated with sodium hydroxide, sodium bicarbonate, and silane to reduce the water uptake capacity of the fiber, hence the suitability of the resulting composites for a wider range of applications. The views upheld by these two reports are perfectly in agreement with the general perspective in this field [14,51–53]. Begum & Islam [19] compared the mechanical strength of natural-FRPCs with glass-FRPCs and established that the volume fraction of the natural fiber must be more to match the strength equivalent provided by glass fiber. This is also akin to the sentiment expressed by Ramesh [54] who reviewed the preparation, properties, and prospects of flax-FRPCs to replace harmful synthetic fibers.

In furtherance of the search for improved performance, Atmakuri et al. [55] investigated the possibility of harnessing the strengths of individual synthetic and natural fibers in a hybrid fiber-based composite with nanoparticles. They alluded to the popularity of hybrid composites made from two different natural fibers compared to the combination of natural and synthetic fibers hosted in the same matrix. The reason for this has not been highlighted in any peer-reviewed literature (to our knowledge). However, several authors have studied the properties of the latter for different applications while reporting a significant improvement. Kumar et al. [50] prepared a hybrid banana and glass fiber-reinforced polypropylene (PP) composite to investigate their tensile, flexural, and impact strengths. They achieved major improvements to the mechanical properties of the composites in line with what AlMaadeed et al. [56] concluded in a study of natural/synthetic fiber-reinforced hybrid PP composites. A more recent work by Sivaranjana & Arumugaprabu [57] reported in favor of thermo-mechanical enhancement in addition to the moisture resistance capacity of the hybrid composites. Apart from this, one of the high points of the hybrid composite is the incorporation of nanoparticles which can enhance its surface properties, fracture toughness, and dynamic mechanical properties. Some of the published articles in this area are summarized in Table 1. There appears to be a strong indication of a deliberate shift from natural to synthetic reinforcing filler materials in the development of polymer matrix composite in the last few years because of the strength advantage they offer. The fact that only about 11% of the reviewed publications in the table are natural filler-based lends credence to the allusion.

Judging from the perspective of corrosion resistance and inherent strengths, it is obvious that natural and synthetic FRPCs are promising biomaterials to replace many conventional ones in the biomedical field. Medupin et al. [7] developed a CNTs-based natural rubber composite for in-vitro orthopedic application. The work pointed out many comparative advantages inherent in using biodegradable polymer composite for developing prosthetic feet in place of non-biodegradable and metallic alternatives. Not only do eco-friendly polymers harvested from renewable sources help to rid the environment of poisonous materials, but also offer tremendous strength and dynamic flexibility requirements for any materials that would sufficiently mimic anatomical feet. Other areas of orthopedic application widely researched include prosthetic sockets with reinforced polymer featuring as the most extensively used materials [67,80,81]. Reinforced thermoplastics are the preferred polymer materials for this in-vitro orthotic and prosthetic application. Shah et al. [82] incorporated CNT fillers into UHMWPE to achieve a smoother material surface for improved tribological properties, particularly the wear resistance of polymers. Their work was based on the general mechanism by which CNT reinforcement enhances the mechanical properties of polymeric matrices. Thermoplastics are conveniently prominent in both orthosis and prosthesis biomedical applications. Furthermore, researchers have also turned to these materials for certain in-vivo orthopedic applications, leveraging the innate strength of some synthetic fillers to strengthen polymers for bone replacement [83]. The ability of CNTs to be functionalized with a multiplicity of organic and inorganic molecules make them an ideal candidate for several biomedical applications. Amurugam and Ju [5] are the few researchers who have affirmed the biocompatibility of CNTs and their suitability for in-vivo use. Therefore, the inertness and biocompatibility, respectively, of both thermoplastics (polymers) and CNTs (fillers) can be combined to develop a resilient composite for bone replacement as evident in many reports.

## 4. CNT-reinforced polymer composites

The superlative properties of CNTs have generated volumes of research publications on their applications following a series of discoveries, post-1991 [84]. It is considered a perfect reinforcing agent for next-generation nanocomposites because of its unique electrical, and thermo-mechanical properties as well as high aspect ratio, exceptional stiffness, and excellent strength. Early adopters of this technology have turned out hundreds of articles on CNT/polymer (nano)composites with the specific purpose of performance enhancement of conventional polymer composites and for applications in the aerospace and other industries requiring high-performance materials [3,85–88]. Salahuddin et al. [89] identified CNTs, among other allotropes of carbon, as common coating materials needed to achieve a strong fiber/matrix interface which is necessary for an improved mechanical property in nanocomposite systems. In a concise submission, they reported CNT as a desirable coating material that can impart the required properties to CNT/polymer composites to accurately control their synthesis to align them in the optimal direction. This, they concluded, can boost the performance of the composites. Arash et al. [23] also canvassed this position when they investigated the mechanical properties of CNT/polymer composite in comparison to its conventional counterparts. Since the mechanical strength of the nanocomposite is dependent on the condition of the filler/matrix interface, they developed a methodology based on the fracture behavior of the nanocomposites to evaluate the elastic properties of the interface. It can, therefore, be concluded that the performance of CNT-reinforced polymer composites is largely dependent on the strength of the interface between the two materials.

Natural rubber nanocomposites exhibit excellent physical, mechanical, thermal, and viscoelastic properties with significant potential for application in modern biomedical devices. It has been well thought-out as one of the best polymer nanocomposites for prosthetic foot application, especially with CNTs as reinforcing fillers [15,41,90]. The Sustainable Development Goals (SDGs) towards which all human activities including engineering manufacturing must be tailored have prompted increased advocacy for use of renewable materials such as natural rubber (the only rubber from a renewable source) which poses fewer dangers to the environment in comparison with thermoplastics and other synthetic rubber.

**Table 1**
Summary of recent studies on CNT-reinforced polymer (nano)composites from 2018 to 2022.

| Host matrix | Reinforcing filler/fiber | Nature of fillers | Focus of study | Findings | Applications | Authors |
|---|---|---|---|---|---|---|
| Natural rubber | MWCNTs | Synthetic | Compounding NR/MWCNT nanocomposite for a prosthetic foot. | Lower filler concentration reinforces natural rubber netter with improved geometrical stability. | Prosthetic foot | [7] |
| Rubber | carbon nanofillers | Synthetic | Fabrication methods of carbon-based rubber nanocomposites and applications | Homogeneous mixing of carbon nanofillers with rubbers was achieved | rubber fabrication | [40] |
| Epoxy Polyester | Natural leaf fiber | Natural | The influence of fiber loading and fiber properties of natural leaf length on mechanical properties of polymer composite | Natural leaf fiber polymer composites are compared favorably to synthetic fiber polymer composites. It is also notable that excess fiber loading and concertation of treatment can affect the strength of the composite. | Varied | [50] |
| Natural rubber | Natural fibers | Natural | Effect of surface treatment on Natural fibers composite | The hydrophilicity of the natural fiber is reduced in the reinforcement and there is an increase in bond with the matrix in the reinforcement due to surface treatment. | Diverse | [51] |
| Natural rubber | Carbon black | Synthetic | Formulation of hybrid natural rubber matrix nanocomposite using carbon black and CNTs. | CB/CNT reinforced NR hybrid NCs exhibit superior physical and mechanical improvements in comparison to the conventional composite | Rubber liners used in acid storage tanks | [58] |
| Silicone | Graphene (GR), CNTs | Synthetic | Strain sensing behaviors of conductive polymer composites using CNTs and GR in silicone rubber (VMQ) composites. | Self-assembled CNTs-GR/VMQ composites have an extremely lower percolation threshold of 0.92 wt% in comparison to CNTs/VMQ composites. | Diverse | [59] |
| NR latex | Cellulosic microfiber | Synthetic | GP/CMF-NR composite sponge. | Increased graphene content causes a significant improvement in the compressive properties of the GCR-10 composite | Piezoresistive sensors and fire-warning sensors | [60] |
| Natural rubber | CNTs | Synthetic | Vibration and damping characteristics of rotating laminated composite hybrid MR elastomer sandwich panel. | CNTs reinforced MR elastomer has a significant influence on the natural frequencies, loss factors, mode shapes, and transverse displacements of the composite sandwich panels. | Transverse vibrations on structures | [61] |
| Natural rubber | Carbon black (CB) | Synthetic | Study on CNT-CB/NR and GO-CB/NR composites | The tendency of the fillers to exist as separate entities helped to improve their dispersion in the NR matrix while enhancing the strain-induced crystallization ability of CB/NR. Modulus at 100% strain as well as tear strength of the composites was significantly upgraded. | Structures | [62] |
| Natural rubber | CNTs | Synthetic | Reduction of the agglomeration and settlement of CNTs in polymer composite using the slurry blending method | Better dispersion of CNTs in the NR and improved tensile strength of the sample by 15.2% were achieved | Rubber industry | [63] |
|  | CNTs, Graphene | Synthetic | Environment remediation through the use of CNT. | The mechanical performance of carbon nanomaterials-based composites got enhanced by the use of Van der Waals force interfacial compounds | Environmental Remediation | [64] |
| Natural rubber | Graphene oxide | Synthetic | Reduced graphene oxide/natural rubber (rGO/NR) composites for multi-sensing applications. | When immersed into tetrahydrofuran for just 2s, rGO/NR offers an improved electric resistance change which decreases linearly with temperature, showing a higher sensitivity in comparison with conventional alternatives. | multi-sensing materials | [65] |

**Table 1** (*continued*)

| Host matrix | Reinforcing filler/fiber | Nature of fillers | Focus of study | Findings | Applications | Authors |
|---|---|---|---|---|---|---|
| Natural rubber | MWCNTS | Synthetic | Deploying natural rubber piezoresistive sensors for sensing interface application. | Low electrical percolation threshold and improved mechanical properties were demonstrated by conducting elastomer and performed excellently as a movement detector. | sensing robots and soft robotic | [66] |
| Polymer | Jute plus carbon | Natural + synthetic | Developing prosthetic sockets for fiber-reinforced polymer. | Reinforcing layers helps to improve the mechanical properties (flexural modulus and maximum shear stress particularly) of the prosthetic socket. | Prosthetic socket | [67] |
| Silicone rubber | $Al_2O_3$, CNTs | Synthetic | Use of CNTs as reinforcing agents for the thermal and mechanical improvement of alumina-filled silicone rubber. | A higher mass fraction of the alumina powder causes higher thermal conductivity of composites. | Diverse | [68] |
| Natural rubber | MWCNTs & carbon black | Synthetic | Enhancing the mechanical properties of CNT-based rubber nanocomposites. | MWCNT contributed significantly to the enhancement of the mechanical properties of natural rubber. | Varied | [69] |
| Natural rubber, styrene-butadiene rubber | MWCNTS | Synthetic | MWCNT-filled natural and synthetic rubber nanocomposites | Good filler–rubber interaction exists at the interface; triggering a good reinforcement effect as well as the improved electrical conductivity of the compounds. | Diverse | [70] |
| Natural rubber | CNT/PEDOT: PSS hybrid | Synthetic | Microfluidic preparation of natural rubber | The fabricated strain sensors demonstrated a high capacity to stretch up to 1275% and high linearity of 1000%, within about 63 ms, and a high resolution of 0.05%. | fabric-sewable wearable strain sensor | [71] |
| Natural rubber | Graphene oxide, ZnO | Synthetic | A study on the interfacial strength of ZnO-modified NR/GO nanocomposites | Mechanical and dielectric properties from neat NR and NR-GO nanocomposites were significantly improved. | Coating in automotive, aerospace | [72] |
| Natural rubber | CNTs, wood-derived carbon scaffold (CS) | Natural + synthetic | Study on thermal integrity of CS/CNT/NR composite. | CS/CNT/NR composite favors high-speed heat transport. | Heat transfer | [73] |
| Polyurethane | CNTs | Synthetic | Production of highly conductive CNT-TPU NC for smart clothing applications | Change of the CNTs content in TPU can control the stress and strain relation in the fibers | Smart Clothing Applications | [74] |
| Natural rubber | Alumina, graphene oxide | Synthetic | Improvement of thermal and mechanical properties of NR composites | The highest rate of thermal conductivity was noticed at 25 wt% F- GA filler content. | Electronic packaging | [75] |
| Thermoplastics | CNTs | Synthetic | CNT-reinforced thermoplastics | CNTs were easily dispersed in the HDPE matrix, resulting in the improved mechanical performance of the composite. | Diverse | [76] |
| Silicone | CNTs, carbon fiber | Synthetic | Information management in space engineering | Silicone adhesion made the EMI rubber corrosion-resistant and 52.3% elongation at break. | Aircraft sealing and shielding against electromagnetic waves | [77] |
| Polymers | Nanoclay | Natural | Nanoclays in polymer-based packaging materials | Nanoclays are a strong enhancer of the thermal, mechanical, and barrier properties of a polymer. | Food packaging | [78] |
| Natural rubber, paraffin wax | CNTs | Synthetic | 2-way shape memory properties of NR/PW blends and nanocomposites | PW-filled NR showed an unusual THF solvent vapor-triggered reversible shape memory system without any external stress and pre-soaking treatment. | Shape memory properties. | [79] |

Poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS).

### 4.1. Mechanical properties of CNT-reinforced polymer composites

To optimize the choice of rubber/nanoparticles (NR/NPs) composite for engineering application, very particular attention must be paid to the behavior of materials under mechanical forces. The mechanical properties of styrene butadiene rubber (SBR)/silica nanocomposites vulcanized by different vulcanizing agents are illustrated in Fig. 4(a)–(c) [91]. This selection process includes comparing mechanical properties under certain service conditions for several candidates and comparing mechanical properties under certain service conditions. When the mechanically stable NPs are distributed in less stable rubber matrices, they impart stability to the polymer composites contingent on the matrix-to-filler ratio. Oleiwi et al. [67] have earlier sought to make rubber systems acquire conductivity by incorporating CNTs into them. The addition of the filler hardens the nanocomposites and hence, the stress–strain

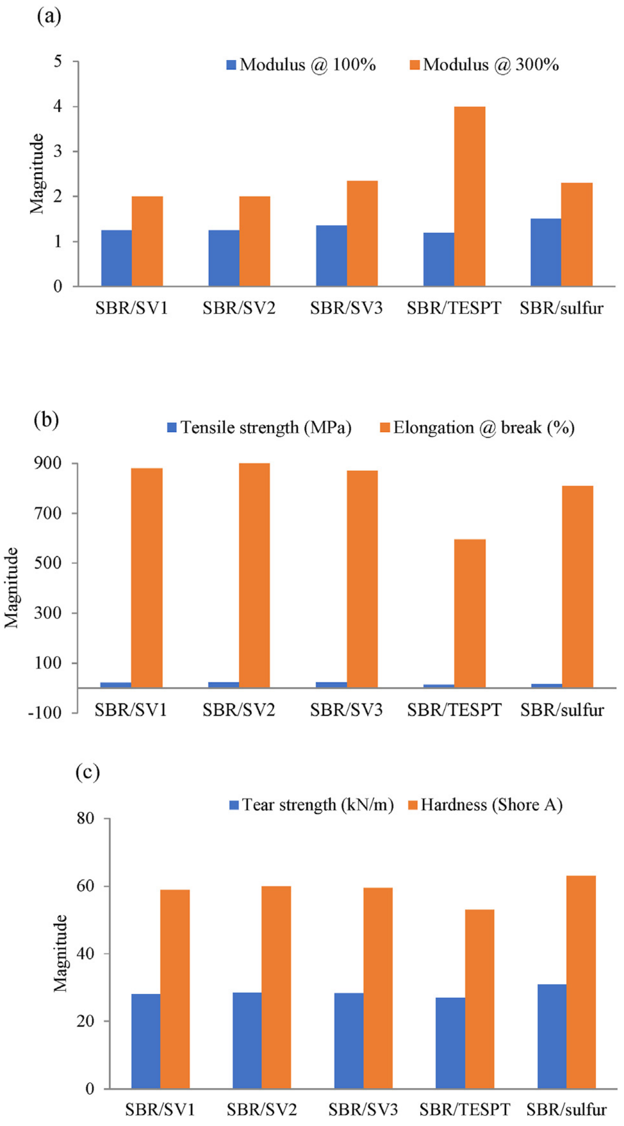

**Fig. 4.** Mechanical properties of SBR/silica nanocomposites: (a) modulus at 100% and 300%, (b) tensile strength and elongation at break, (c) strength and hardness [91].

curves became steeper compared to the virgin rubber system in a similar fashion as shown in Fig. 4(a). These remarkable drops were noticed with a further increase in MWCNT content beyond the threshold of 3 phr [8,41]. Additionally, the dispersion of NPs in rubber helps to stiffen and harden the composites because of their higher mechanical performance. It was found that a lower concentration of synthetic fillers favors an improved tensile strength of 6.02 MPa; hence a better ability to withstand the tensile load.

Similarly, Hussain et al. [113] reported that the mechanical properties of rubber nanocomposites respond to changes in temperature. This, according to them, could result in deterioration at elevated temperatures. They investigated tensile stress–strain behaviors at room temperature, 60 °C, and 100 °C to determine the extent of the influence of temperature on tensile strength, strain at break, and stresses at 100% and 300% strains. Their study verified earlier reports of decreases in tensile strength, strain at break, and stresses at 100% and 300% strains with temperature as a result of weakened intermolecular interactions. In the same vein, the reinforcing effect and improved crosslinking density induced by increasing the volume fraction of fillers caused an increase in tensile strength and stresses at 100% and 300% strains.

As shown in Fig. 4(b), the behavior of filled natural rubber is best described by the distribution of MWCNTs to cut the existing crosslinks and hence reduce the elastic properties of the nanocomposites. The behavior, however, is more obvious with higher percentages of elongation where the empty NR possess the lowest elongation at break [91]. The results are consistent with the reduction in high elastic properties of the NR compound. In keeping with previous findings by Arumugam and Ju [5] and Li et al. [92], the nanocomposite with the lower filler concentration showed an improved uniform dispersion and, therefore, better crystallization and cross-links, resulting in an improved module. This is evident in the different percentages of the length shown in Fig. 4(a).

Furthermore, the need for environmentally stable materials necessitated the physical test consistent with nanocomposite (Fig. 5). Water absorption curves are illustrated in Fig. 5(a) while the rate of absorption was presented in Fig. 5(b). Consistent water uptake noticed for the first 30 days and an eventual reduction and total stop were linked to the diffusion phenomenon in which water molecules permeate the composite material. During the process of mixing the filler with the matrix phase, hydrophilic fillers are coated with the rubber phase and remain isolated from adjacent fillers. As such, it becomes difficult for water molecules to permeate the interstices which must have been closed, in this case, owing to the method of production, compression molding. According to Li et al. [92], the improvement of interfacial adhesion between MWCNTs and NR matrix is achieved by surface treatments that make the filler–matrix interaction more consistent. Consequently, load transfer from NR matrix to filler is engendered and favors stress flow throughout the composite, resulting in good viscoelastic properties.

Dynamic mechanical analysis (DMA) is a popular method used to estimate the viscoelastic performance of polymer composite materials. Its performance depends on fiber volume, orientation, additives like fillers, and compatibilizers such as sodium dodecylbenzene sulfonate [7]. This method is critical for establishing wide-ranging temperature-dependent material data for materials that would be subjected to dynamic loading, for example, human gait. The plots for storage modulus (E′), loss modulus (E″), and damping factor (tan $\delta$) of neat rubber, natural rubber reinforced carbon black (NR-CB), bamboo cellulosic particles (NR-BNC), coconut husk cellulosic particles (NR-CHNC) nanocomposites were investigated by Oboh et al. [93] are illustrated in Fig. 6. Ramesh [54] reported DMA experiment following a similar procedure adopted by Medupin et al. [7] and Oboh et al. [93]. It is obvious from the curves that integration of MWCNTs, like other stiffer fillers, causes increased E′ and thus weakens as the temperature rises. Empty NR vulcanisate presented the least E′ which is an indication of matrix-to-filler stress transfer according to Atmakuri et al. [55]. As filler loading increases, these values also tend to grow and peak with higher filler material. To the degree that the filler phase is stiffer than the matrix phase, E′ is always higher with MWCNTs filler (Fig. 6(a)). In another study, Li et al. [92] confirmed that increased E′ and E'' indicate that MWCNTs constitute a barrier to the NR chains movement, resulting in a lower elasticity and higher hardness of NR/MWCNTs nanocomposites. Using the tensile mode DMA, Sethulekshmi et al. [88] evaluated the thermo-mechanical stability property of $Al_2O_3$ and $SiO_2$-filled nano/micro composite samples. Their results indicate that nano and micro-sized fillers improve the mechanical property of the composites, thereby improving the glass transition temperature ($T_g$). It was found that the micro-composite specimens display a high E′ beyond the glass transition temperature. The results, however, were not as straightforward for the nanocomposites as can be seen in Fig. 6(b).

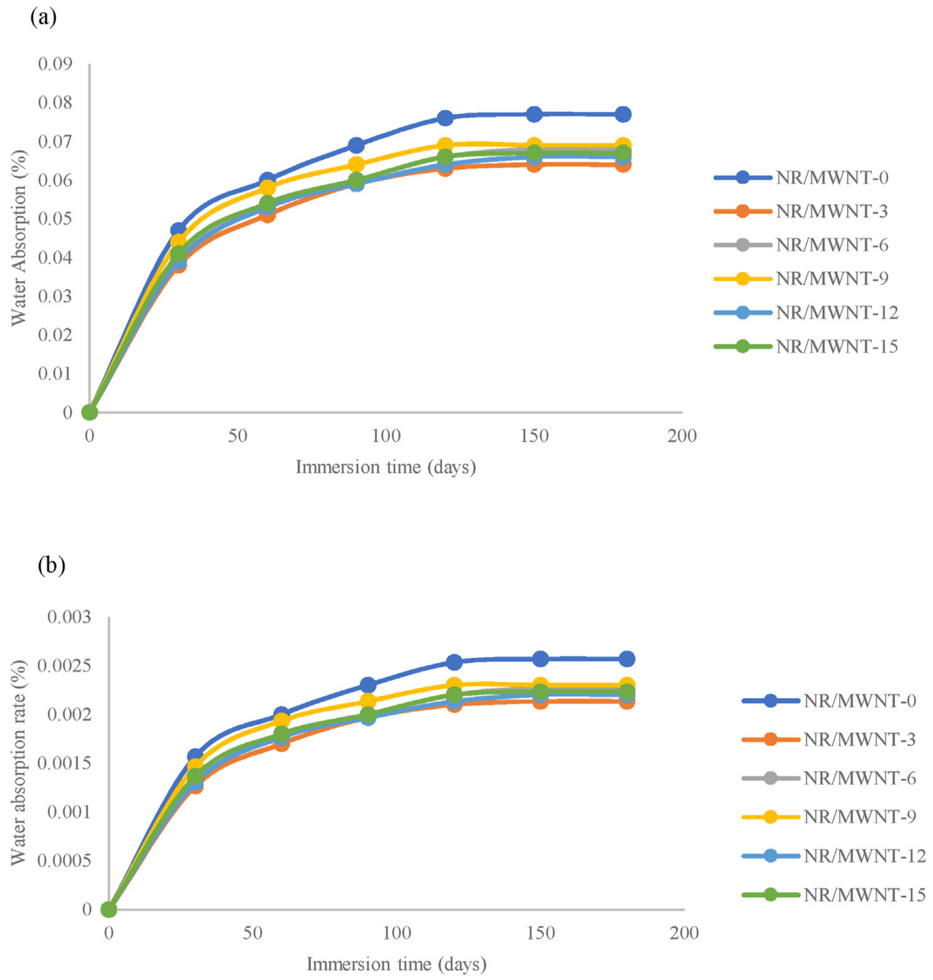

**Fig. 5.** Physical properties (a) Water absorption (b) Water absorption rate [7].

### *4.2. Thermal properties and morphology of nanoparticles reinforced rubber*

The thermographs of TGA and the corresponding derivative thermogravimetry (DTG) of MWCNTs-reinforced natural/synthetic rubber composites are shown in Fig. 7. TGA is used to determine the quality of fiber from its characteristics [54]. CNTs were strongly thermally stable and light weight loss at 650 °C [7,41], which was always important to improve the thermal stability of CNT/NR composites. The introduction of MWCNTs into NR compound shows substantial changes in the $T_{onset}$ of the nanocomposites. The decomposition temperature of nanocomposites is between 250 and 600 °C (Fig. 4(d)), without changing the wt% of nanocomposites.

In conclusion, the thermal stability of NR nanocomposites is improved by the addition of CNTs. This is a general behavior of all FRPCs (these include but are not limited to thermoplastic, thermosets, and different types of nanoparticles as fillers), this could be attributed to the combination of the nanoconfinement effect and the barrier effect of the new nanofillers [52,75,78,87,94].

Similarly, morphological examination of polymer nanocomposites is often carried out to better appreciate the extent of polymer/filler interaction at the interface. The surface of different composites was observed by Guo et al. [62] using Scanning Electron Microscopes (SEMs), as shown in Fig. 8. NR composite devoid of any form of reinforcing fillers exhibited a smooth surface as illustrated in Fig. 8(a). However, as fillers were being introduced, white spots indicating CB particles show up with unfilled spots still widespread as indicated by red eclipses (Fig. 8(b)). The white spots continue to grow in density as other fillers were added. CB/CNT/GO filled rubber had the most reduced red ellipses because fillers got uniformly dispersed making the system stiffer and much stronger. The degree of aggregation of CB was significantly reduced as shown in Fig. 8(d).

The samples were further viewed under Transmission Electron Microscope (TEM) as illustrated in Fig. 9. The black patches in Fig. 9(a) are ZnO particles [62]. Many CB agglomerates were spotted in Fig. 9(b) as black spots in red ellipses. Gou et al. [62], like many other researchers, reasoned that the spontaneous irreversible behavior of CNTs and other nanoparticles, causing a reduction in their surface energy, was responsible for the agglomeration. These agglomerates are said to be suspected sites for the initiation of microcracks which could lead to quick failure of the rubber composites during the fatigue process and other dynamic loading or stresses [13,62]. Thin and lengthy red triangles are CNTs (Fig. 9(c)) and GO (Fig. 9(d)) scattered among the round CB particles. The improvement of the bonding at the interface between the filler and the rubber host is attributed to the esterification mechanism and filler breakage resulting from the mechanical manufacturing process. As a result, stress distribution between the two phases is improved, favoring improved mechanical performances.

## 5. CNT-reinforced natural rubber nanocomposites

Despite evidence of remarkable success in composite development for a wide range of applications, there is a dearth of literature concerning the reinforcement of natural rubber with CNTs for biomedical purposes. Having experimented with different reinforcing agents (natural and synthetic) for polymer matrix composites, it was necessary to take the search to the next level of using materials from renewable sources in compliance with the clamor for sustainable manufacturing. The feasibility of using poly(methylmethyl-acrylate)/silicone rubber (PMMA/SR) as a prosthetic foot material was explored by Hadi and Oleiwi [95] to improve the resistance of the polymer mixture. They observed a lack of flexibility in the existing prosthetic foot systems to enable amputees to carry out simple routine activities such as kneeling and bending over to wear shoes. Disadvantages associated with initial prosthetic materials, such as weight, durability, and irritation by moisture was highlighted. The study, which should provide the basis for comparing PMMA/SR mixture strengthened by CFs with existing prosthetic foot materials, was not sufficient as the same conventional materials and methods as those used by previous researchers were used. Similarly, Hadi and Oleiwi [96] used PMMA/SR polymer mixture as a base matrix, and CF-reinforced polymer composites. Improvement of flexibility strength was their objective. PMMA polymers were mixed with SR and formed into binary mixtures and reinforced with CF. Improvements were reported in the flexibility, and flexibility modulus as reinforcement increased from 5 to 15% CF. According to the researchers, these improvements support the dorsiflexion of polymer materials for prosthetic feet application. Improvement of flexural strength is also said to have the ability to improve the application of the material. Hadi and Oleiwi [96] were unable to justify their claims that the material was suitable for prosthetics in a known static or dynamic test method.

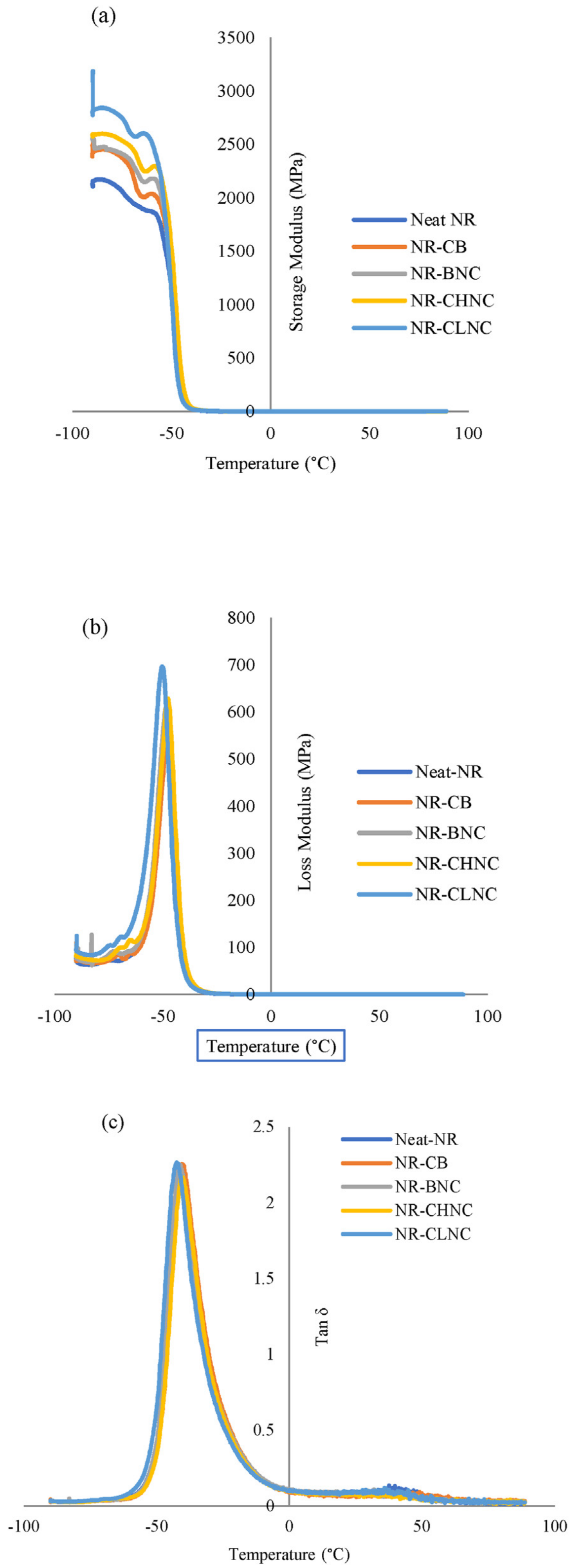

**Fig. 6.** DMA thermograms of NPs reinforced rubber (a) Storage modulus (b) Loss modulus (c) Tan delta [93].

Park et al. [97] investigated the effect of CNT diameter on the physical properties of CNT/SBR nanocomposites using the melting mixture process for dispersing CNT in polymer with nitrogenic acid ($HNO_3$) as the dispersal agent. Significant increases in curing time, minimum and maximum torque, and stress resistance of larger diameter CNTs were reported. However, for smaller-diameter CNTs, curing time decreased with the addition of CNTs. Zhou et al. [98] explored the combination of the spray drying method with the mechanical mixing process for the effective distribution of CNTs in styrene rubber (SBR) in the presence of sodium dodecylbenzene dispersants to design a new manufacturing method and improved mechanical properties for CNT/SBR nanocomposites. The formulations used in their research were SBR 100 phr, 1 phr of vulcanizing reagent, and 0–60 phr of CNT (10 phr interval). The weight proportion of the CNT in the composites is between 0 and 34.8%. A new path for the modification and reinforcement of polymers using large amounts of CNTs with better tensile, tear, and SBR hardness was reported. This conclusion ran contrary to the submission by Kearns and Shambaugh [99] and Hussain et al. [100] who reported that polymers have the capacity for no more than 0.5 wt% of CNT reinforcement. However, their work abruptly ended without considering any specific application and, therefore, raised questions about the claim that SBR can interface with up to 60% of CNTs without agglomeration problems.

Chahravarthy et al. [101] studied the compatibility of biomedical materials for knee prostheses with materials with the same characteristics as ultra-high molecular weight polyethylene (UHMWPE). They modeled and analyzed the wear of UHMWPE prosthetic knee joints that can withstand various loads inherent in mobility. The model's biomechanical analysis showed that knee joint load condition at full load was 3500 N, a value that is lower than the foot fluttering and stepping load conditions are 4.48 kN and 4.023 kN respectively. While they concluded that the virtual prototype was suitable for the replacement of the prosthetic knee, they pointed out that the design could be further optimized for less material usage. Recognizing that nanomaterials provide a better

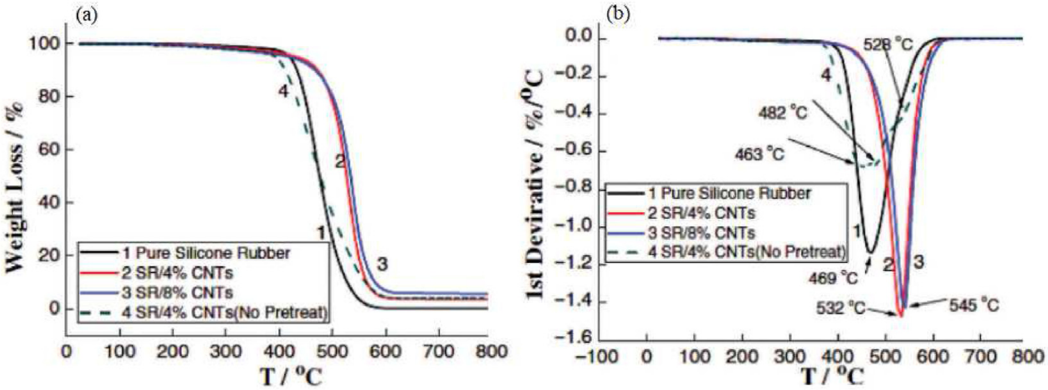

**Fig. 7.** Thermogravimetric analysis (a) TGA plots of composites (b) DTG of composites [41].

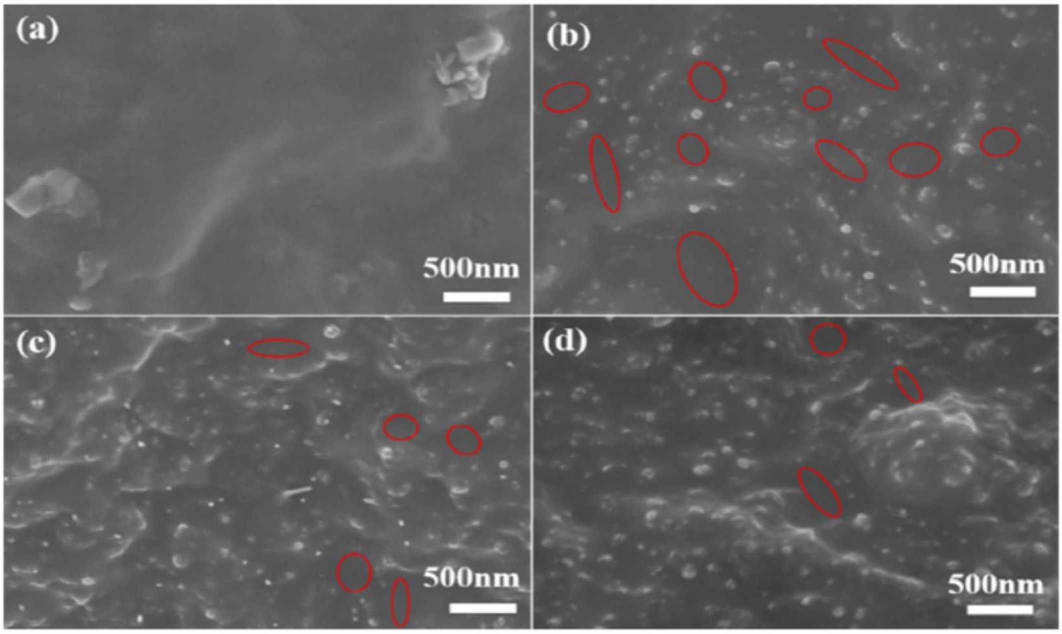

**Fig. 8.** SEM images (a) NR (b) CB/NR (c) CNT-CB/NR (d) GO-CB/NR composite [62].

option in terms of superior mechanical properties requires the shift from conventional materials to polymer composites meant for biomedical applications. Mohammed et al. [14] presented a critical study of the distribution of MWCNTs in natural rubber latex (NR-latex) using surfactants containing phenyl ring components [14]. In their research, the group of scientists confirmed that the stabilization of nanofillers in matrices may be a serious challenge in developing polymer nanocomposites. The use of CNTs, especially MWCNTs, is increasingly popular for those interested in polymer composites based on CNTs. However, the difficulty encountered during the dispersion of CNTs in polymer matrices remains to be tackled. As a result, further experimental treatment of fillers has been suggested by other studies. Of the two commercially available ion surfactants often used to stabilize CNTs in host polymers (sodium dodecyl sulfate, $NaC_{12}H_{25}SO_4$, and sodium dodecylbenzenesulfonate, $C_{18}H_{29}NaO_3S$), it was concluded that $C_{18}H_{29}NaO_3S$ has a better capacity due to the phenyl ring of the former. Although the study proposed a molecular design criterion for the stabilizer of NR-latex nanotubes, it did not apply any applications related to the loading capacity of the composite.

Muter and Mugar [102] reported on a study on the development of natural rubber mixtures with different thermoplastics (in this case polyethylene and polystyrene) and fillers. The mechanical and chemical properties of natural rubber mixtures reinforced with black carbon and nanocarbon at different ratios have been studied with compression molding rubber mixtures at150±2 °C for 20 min using an electrically heated hydraulic press. The examination of vulcanisates revealed that carbon black particles were not easily distributed in rubber mixtures; Therefore, a strong carbon—polymer interaction that is crucial to achieving the maximum possible tensile strength has not been achieved. It was also impossible to uniformly disperse nano-carbons in a polymer matrix over 5 phr. When nanocarbon reinforcements were raised above 5 phr, tensile strength fell significantly. They concluded that binary mixtures of rubber matrix composites provide excellent resistance to the chemical atmosphere. Their report set out the possibility of obtaining NR/PE and NR/PS mixtures with carbon black and nanocarbon reinforcement for loading applications with excellent aging resistance. However, they fell short of achieving the required optimal mechanical properties. No dispersion agents were

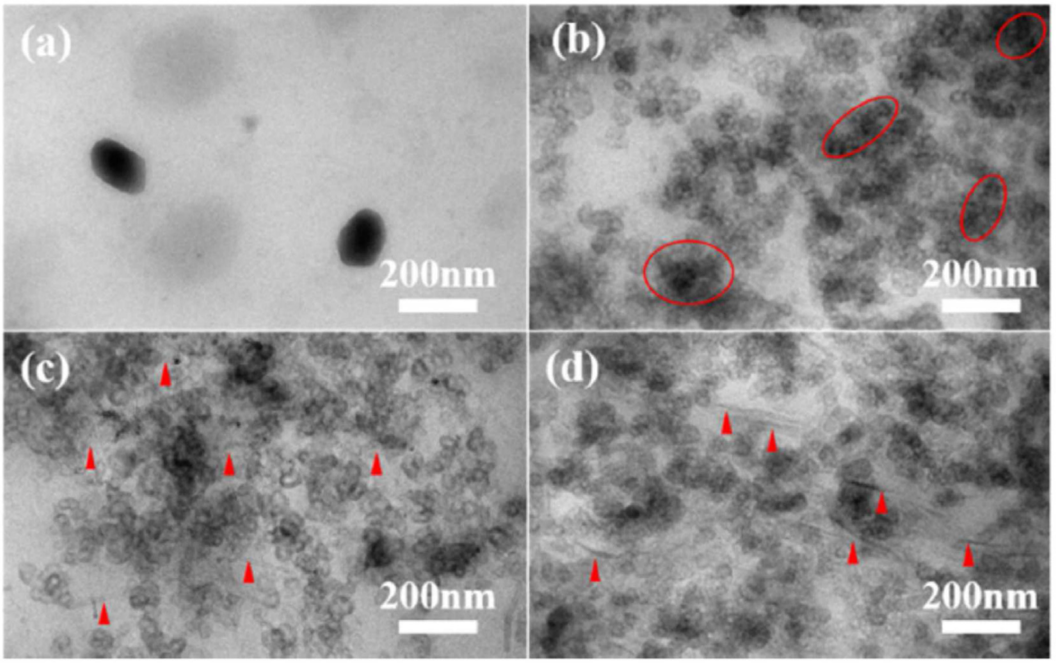

**Fig. 9.** TEM images of (a) NR (b) CB/NR (c) CNT-CB/NR (d) GO-CB/NR composites [62].

used in their work to break the current van der Waals attraction power between individual carbon particles. This leaves a gap in their work and demands more research.

Similarly, Sagar et al. [103] investigated the effects of MWCNT variations (0.1, 0.3, 0.5, and 1.0 wt%) on thermal transport during phase transition temperature and mechanical characteristics of the NR matrix. They developed NR vulcanization process but provided little information on the characteristics of MWCNTs. Again, this leaves a huge gap in their work, as it raises questions about the uniform distribution of the components of the nanocomposites. This is because only shear mixing techniques have proved extremely insufficient to achieve a homogeneous interaction of filler and matrix, as Sagar et al. [103] pointed out. Quite little is known about how much filler concentrations used in their study can achieve good NR reinforcement for dynamically induced load associated with the prosthetic foot. Thus, it can be deduced from the literature that the selection of materials used can influence the mechanical properties of polymer composites regarding their suitability for biomedical applications [104]. One of the main obstacles to the development of polymer nanocomposites is the aggregation of fillers [97,98]. When CNTs are involved, the challenge becomes more serious [100,105]. Pitkin [106] claimed that attention has been diverted from the use of metals and wood to polymer nanocomposites for biomedical purposes due to their weight advantage in combination with the manufacturing costs and, therefore, sustainability and affordability for target users. Similarly, CNTs have been used as reinforcement fillers for high strength, low density, and high aspect ratios (34, 105) in recent years, and the extensive area it provides for interaction with the matrix phase and the interfacial interaction.

All these reports present a common conclusion that natural and synthetic fiber-reinforced polymer composites offer great prospects for biomedical applications, especially for prosthetic feet. While these and other studies show a positive correlation between filler contents and improvements in mechanical properties, there is still a lot of work to be done to draw scientific conclusions on the biocompatibility of these devices made from various CNTs/natural rubber nanocomposites for both in vitro and in vitro applications.

## 6. Current trend in CNT/natural rubber nanocomposites

CNTs-reinforced polymer nanocomposites have become an essential component of today's prosthetic devices owing to their unrivaled strength-to-weight qualities [81,107–109]. The consideration for less expensive but financially more viable solutions using renewable and sustainable materials is currently driving the conversation. The largest number of below-knee amputees which constitute the larger percentage of users of prostheses are domiciled in low-income countries around the world. Therefore, the need to develop tailored materials that will address the concerns expressed by the people and the environment is non-negotiable. Following this, interest to provide a research agenda for the near future development of biomedical devices has continually grown. Mensah et al. [41] reviewed certain challenges that seem to undermine the applicability of CNT-reinforced elastomeric nanocomposites. They identified areas requiring continued studies including manufacturing techniques and physics of interactions between CNT and elastomer, as well as hybrid systems. To address some of the challenges highlighted by Mensah et al. [41], Gao et al. [63] developed a slurry blending method to ensure homogeneous dispersion of CNTs in natural rubber. Their findings suggest that the novel method is to be preferred to the latex blending method because it stabilizes thermal conductivity and improved the tensile strength of the composite by 15.2%. This was discussed extensively in the earlier sections.

Most of the studies on nanofiller-reinforced elastomers are tailored toward the mechanical, physical, and thermal properties of rubber nanocomposites. Vulcanization on a double roll mill (closed or open) is the most popular methodology for processing rubber composites and ensuring that the filler materials get homogeneously dispersed in them [7,58,63,70,71,103]. Some of the popular destinations of publications in CNT/polymer nanocomposites are Composite Science and Technology Journal, Polymers Journal, and Materials Journal among others. Of all the literature available in this area, none (to our knowledge) prioritizes sustainability in their works. However, it is important to pay closer attention to how manufacturing activities in this field impact the environment and human life.

## 7. CNT-reinforced NR nanocomposites development: challenges, future and economic prospects

Given the volume of literature on the applicability of CNT/polymer nanocomposites across diverse fields including biomedical, it is appropriate to assess the sustainability perspective which is scarcely reported in existing peer-reviewed publications, and the opportunities that exist in this research. Researchers in this field have explored the use of various materials, ranging from natural to synthetic, as polymers and fillers with varying degrees of success [64,66,76]. The demand for commercial carbon-based nanomaterials in high-performance applications should also stimulate more interest in sustainability advocacy and involvement. This is a huge gap in this field of study that has been highlighted in this review.

Players in this field are often faced with the initial challenge of having to pay little or no attention to the economic dimension of their activities but are obsessed with just value proposition. And except there is a deliberate attempt to address this concern, it could remain unattended and completely eclipsed by other pressing considerations. However, when CNTs are involved, the cost must be factored into the conversation. The biggest bane of success in the business aspect of CNT-based nanocomposites, apart from the cost of production, remains the difficulties encountered in ensuring good filler dispersion in the matrix. Since the products are expected to dominate the market owing to their comparative advantages, the cost must be prioritized. Therefore, the cost of raw materials and manufacturing activities constitute the major components in this consideration.

While the packaging industry is dominated by nano clay composites because of the good amount of barrier properties they offer over others [78], the polymer nanocomposites market is dominated by CNTs with MWCNTs and SWCNTs widely used in the automotive and electrical and electronics industries [110]. It is also reported that the automotive and aerospace ranked among the largest destinations for the polymer nanocomposites raw materials market in 2018. The biomedical sector, which is the main target of this review, is also being revolutionized by the speedy adoption of polymer-based materials to replace conventional materials in some applications including prosthesis and orthosis. Whereas other areas of the market are already being crowded by heavyweights in the industry, there is yet a big prospect in the biomedical segment. Hence, it becomes much economically safer to play with cost in this area because of the volume of demand and nature of products when compared to areas that concern day-to-day demands. Some of the areas of applications are highlighted in Fig. 10.

The most predominant among the materials used as host matrices for CNT are thermoplastics. They are cheaper than elastomeric materials which are more elastic and better suited in areas where energy absorption and dissipation quality are expected to take center stage [7]. CNT/NR nanocomposites appear to be the least researched nanocomposites. It is expected to break into the biomedical market soon making medical devices more affordable in low-income countries. Until recently, there are no studies dedicated to the social perspective of CNT/NR nanocomposites for prosthetic application. Amsan et al. [114], in a review of the cost and challenges of prosthetic leg development and usage, observed that the rise in the demand for prostheses was a result of the desperate

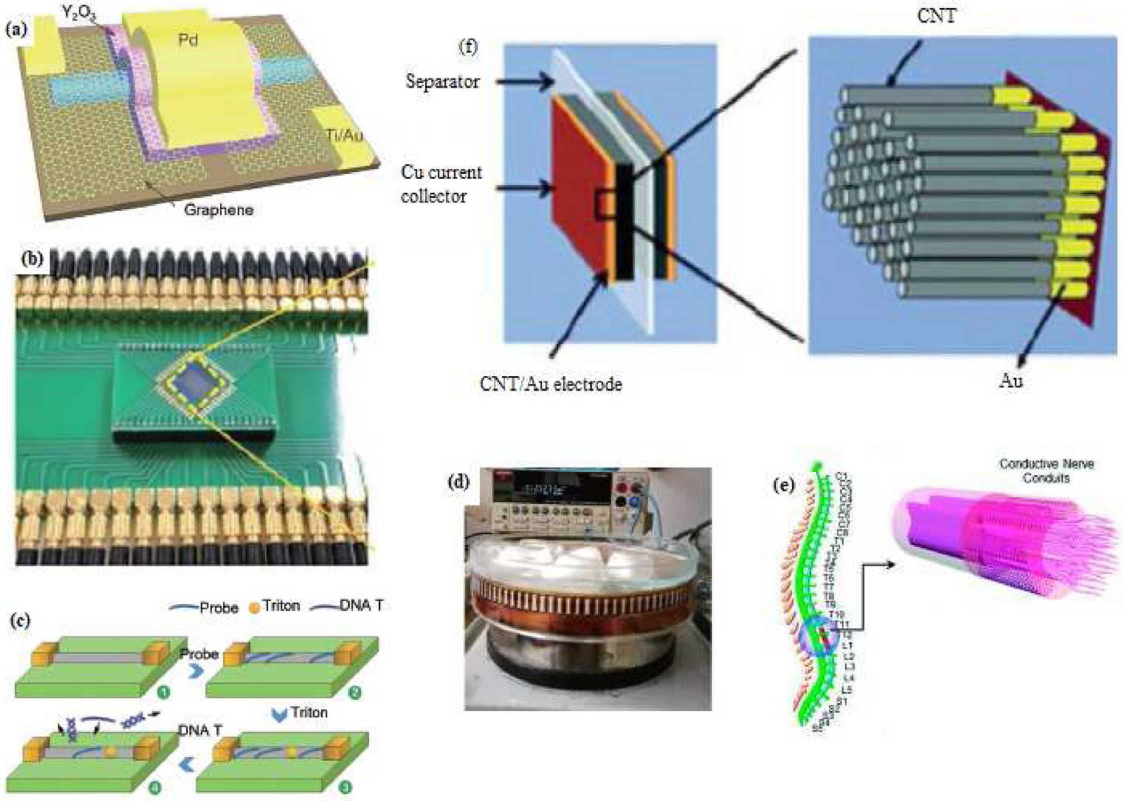

**Fig. 10.** Carbon nanotubes-based devices and applications (a) architecture of CNT-based transistor (b) A floated-gated FET arrays based on s-SWCNT network film (c) CNT-based chemical-resistor for DNA sensing (d) Thermoelectric power generator with p-doped SWCNT (e) Conductive nerve conduits for spinal cord injury treatment OPF-CNTpega hydrogel (f) A super capacitor device with CNT/Au as electrodes [111,112].

quest for improved quality of life by amputees. They assert that the quality and cost-effectiveness of new entrant prostheses are vital to their acceptance in the already competitive market. Okorie et al. [33] added that lower price points could be the fastest economic access for new products into the marketplace. Based on the willingness of amputees to adopt the new material, Huntjens & Kemp [115] concluded that increased social welfare is achievable by championing the philosophy of homo-centrism without compromising eco-centrism.

In this consideration, it is pertinent to pay attention to the complexity of the human environment. While some will swiftly adopt a new prosthetic technology on account of competitive cost and durability, others base their decision to either accept or reject such innovation on the societal image. Amsan et al. [114] evaluated the price level for existing prostheses across many countries in Europe and reported a few: The typical cost of the prosthesis is between $910 and $1138 in Malaysia, around €18,616 in Italy, and even more in America and Australia. Factors like the incorporation of the electronic control system as well as geography could affect market price. A few other factors reported are age, comfort, aesthetical features, and attachments. Cost considerations, no doubt, affect amputees' response to the prostheses market. This review, therefore, offers a new and affordable solution for CNT/NR nanocomposites. Research interests, if intensified in this area, will flood the prosthetic market with much cheaper and more durable artificial feet. Natural rubber, which is a major raw material for the polymer nanocomposite, is much cheaper than other high-performance materials used for the manufacture of artificial limbs.

Whereas eco-centrism comes before all other considerations in any sustainable activities in human society, most of the host matrices used for the manufacture of polymer nanocomposites are synthetic polymers from non-renewable sources and largely non-biodegradable. This runs contrary to SDG's goal 12 on sustainable production and consumption, which implies the production and use of products and services in such a fashion that is socially advantageous, economically feasible, and ecologically benign over their whole life cycle. It is against this background that natural rubber is to be preferred to synthetic polymers in the production of several biomedical devices. Therefore, by embracing the use of CNT/NR nanocomposites for the manufacture of most biomedical devices, we contribute in no small measure to the preservation of the environment in compliance with the Sustainable Development Goals thereby making the environment more habitable to both animals and humans.

## 8. Conclusion

In response to the promotion and restoration of quality of life (QoL) for people living with amputation, a solution-based review centered on an economic, social, and environmental tripod approach has been proposed. So far, Natural rubber is preferred to other polymers in nanocomposite development as the only renewable rubber for this purpose. This study has established an understanding of the interaction between carbon nanotubes (CNTs), other nanofillers, and host matrices as reinforcing materials in polymers. Various techniques for the development of polymer-reinforced nanocomposites have also been adequately summarized in this review.

In addition, it has been identified in this review that several studies in the past focused on providing immediate solutions to address physiotherapical challenges in humans with little or no consideration for the long-term impact of the manufacturing activities adopted, and materials used on both the environment and human life. Given this finding, several manufacturing methods for organic and synthetic-reinforced polymer nanocomposites have been explored and analyzed in this study from a sustainability perspective. This review proposed sustainable manufacturing procedures for rubber nanocomposites, CNTs-reinforced nanocomposites, and properties of polymer nanocomposites for biomedical applications. Current trends in CNTs/NR nanocomposites were discussed with a strong advocacy for sustainability in the development of CNTs/NR nanocomposites. This study provides a platform for researchers in the field to explore sustainable opportunities for the development of CNT-reinforced NR nanocomposites for use in the biomedical industry.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

The authors are grateful to the National Research Fund (NRF) under the aegis of the Tertiary Education Trust Fund (TET Fund), Nigeria, No: TETF/DR&D/CE/NRF2020/CC/09/VOL.1, the National Research Fund (NRF) of South Africa for funding this research, and Lawrence Berkeley National Laboratory, CA, United States specifically for supporting the open access publication of this research.

## References

[1] M.N.O. Sadiku, T.J. Ashaolu, A. Ajayi-Majebi, S.M. Musa, Future of nanotechnology, Int. J. Scient. Adv. (2) (2021) 2, https://doi.org/10.51542/ijscia.v2i2.9.

[2] M. Patel, B. Pardhi, S. Chopara, M. Pal, Lightweight composite materials for automotive - a review, Int. Res. J. Eng. Technol. (2020) 41–47. www.irjet.net.

[3] M. Abdalla, D. Dean, M. Theodore, J. Fielding, E. Nyairo, G. Price, Magnetically processed carbon nanotube/epoxy nanocomposites: morphology, thermal, and mechanical properties, Polymers 51 (7) (2010) 1614–1620, https://doi.org/10.1016/j.polymer.2009.05.059.

[4] B.V. Ramnath, C. Parswajinan, C. Elanchezhian, S.V. Pragadeesh, P.R. Tankishore, V.A. Sabarish, Review on CNT reinforced aluminum and magnesium matrix composites, Appl. Mech. Mater. 591 (2014) 120–123.

[5] S. Arumugam, Y. Ju, Carbon nanotubes reinforced with natural/synthetic polymers to mimic the extracellular matrices of bone - a review, Mater. Today Chem. 20 (2021), https://doi.org/10.1016/j.mtchem.2020.100420.

[6] S. Farah, D.G. Anderson, R. Langer, Physical and mechanical properties of PLA, and their functions in widespread applications — a comprehensive review, Adv. Drug Deliv. Rev. 107 (2016) 367–392, https://doi.org/10.1016/j.addr.2016.06.012.

[7] R.O. Medupin, O.K. Abubakre, A.S. Abdulkareem, R.A. Muriana, A.S. Abdulrahman, Carbon nanotube reinforced natural rubber nanocomposite for anthropomorphic prosthetic foot purpose, Sci. Rep. 9 (1) (2019), https://doi.org/10.1038/s41598-019-56778-0.

[8] R.O. Medupin, O.K. Abubakre, A.S. Abdulkareem, R.A. Muriana, S.A. Lawal, Dimensional and thermal reliability of multi-walled carbon nanotube filled natural rubber nanocomposites, Int. J. Eng. Res. Afr. 51 (2020) 177–189, https://doi.org/10.4028/www.scientific.net/jera.51.177.

[9] C.F. Hovorka, G.F. Kogler, Y.H. Chang, R. Gregor, Material properties and application of biomechanical principles provide significant motion control performance in experimental ankle foot orthosis-footwear combination, Clin. Biomech. 82 (2021), https://doi.org/10.1016/j.clinbiomech.2021.105285.

[10] N. Saifuddin, A.Z. Raziah, A.R. Junizah, Carbon Nanotubes: A review on structure and their interaction with proteins, 2013.

[11] A. Takakura, K. Beppu, T. Nishihara, A. Fukui, T. Kozeki, T. Namazu, Y. Miyauchi, K. Itami, Strength of carbon nanotubes depends on their chemical structures, Nat. Commun. 10 (1) (2019) 1–7, https://doi.org/10.1038/s41467-019-10959-7.

[12] H. Zheng, W. Zhang, B. Li, J. Zhu, C. Wang, G. Song, G. Wu, X. Yang, Y. Huang, L. Ma, Recent advances of interphases in carbon fiber-reinforced polymer composites: a review, Compos. B Eng. 233 (2022), https://doi.org/10.1016/j.compositesb.2022.109639.

[13] R.O. Medupin, O.K. Abubakre, A.S. Abdulkareem, R.A. Muriana, I. Kariim, S.O. Bada, Thermal and physico-mechanical stability of recycled high-density polyethylene reinforced with oil palm fibres, Eng. Sci. Technol., Int. J. 20 (2017) 1623–1631.

[14] L. Mohammed, M.N.M. Ansari, G. Pua, M. Jawaid, M.S. Islam, A review on natural fiber reinforced polymer composite and its applications, Int. J. Polym. Sci. (2015), https://doi.org/10.1155/2015/243947.

[15] S. Frackowiak, J. Ludwiczak, K. Leluk, Man-made and natural fibres as a reinforcement in fully biodegradable polymer composites: a concise study, J. Polym. Environ. 26 (12) (2018) 4360–4368, https://doi.org/10.1007/s10924-018-1301-9.

[16] H.T.N. Kuan, M.Y. Tan, Y. Shen, M.Y. Yahya, Mechanical properties of particulate organic natural filler-reinforced polymer composite: a review, Compos. Adv. Mater. 30 (2021), 263498332110075, https://doi.org/10.1177/26349833211007502.

[17] P.A. Gunatillake, R. Adhikari, N. Gadegaard, Biodegradable synthetic polymers for tissue engineering, Eur. Cell. Mater. 5 (2003) 1–16, https://doi.org/10.22203/eCM.v005a01.

[18] Y.G. Thyavihalli Girijappa, S. Mavinkere Rangappa, J. Parameswaranpillai, S. Siengchin, Natural fibres as sustainable and renewable resource for development of eco-friendly composites: a comprehensive review, Front. in Mater. 6 (2019) 1–14, https://doi.org/10.3389/fmats.2019.00226.

[19] K. Begum, M.A. Islam, Natural fibre as a substitute to synthetic fibre in polymer composites: a review, Res. J. Eng. Sci. 2 (3) (2013) 46–53.

[20] W. Wang, Y. Zhu, S. Liao, J. Li, Carbon nanotubes reinforced composites for biomedical applications, BioMed Res. Int. (2014), https://doi.org/10.1155/2014/518609.

[21] F.S. Shahar, M.T. Hameed Sultan, S.H. Lee, M. Jawaid, A.U. Md Shah, S.N.A. Safri, P.N. Sivasankaran, A review on the orthotics and prosthetics and the potential of kenaf composites as alternative materials for an ankle-foot orthosis, J. Mech. Behav. Biomed. Mater. 99 (2019) 169–185, https://doi.org/10.1016/j.jmbbm.2019.07.020.

[22] A. Martone, G. Faiella, V. Antonucci, M. Giordano, M. Zarrelli, The effect of the aspect ratio of carbon nanotubes on their effective reinforcement modulus in an epoxy matrix, Compos. Sci. Technol. 71 (8) (2011) 1117–1123.

[23] B. Arash, Q. Wang, V.K. Varadan, Mechanical properties of carbon nanotube/polymer composites, Sci. Rep. 4 (2014).

[24] E.G. Barathi Dassan, A. Anjang Ab Rahman, M.S.Z. Abidin, H.M. Akil, Carbon nanotube-reinforced polymer composite for electromagnetic interference application: a review, Nanotechnol. Rev. 9 (1) (2020) 768–788, https://doi.org/10.1515/ntrev-2020-0064.

[25] M.D. Kiran, H.K. Govindaraju, T. Jayaraju, N. Kumar, Effect of fillers on mechanical properties of polymer matrix composites, Mater. Today Proc. 5 (10) (2018) 22421–22424, https://doi.org/10.1016/j.matpr.2018.06.611.

[26] N.F. Zaaba, H. Ismail, Thermoplastic/natural filler composites: a short review, J. Phys. Sci. 30 (2019) 81–99, https://doi.org/10.21315/jps2019.30.s1.5.

[27] T.G.Y. Gowda, M.R. Sanjay, K.S. Bhat, P. Madhu, B. Yogesha, T.G.Y. Gowda, M.R. Sanjay, K.S. Bhat, P. Madhu, Polymer matrix-natural fiber composites: an overview Polymer matrix-natural fiber composites: an overview, Cogent Eng 47 (2018), https://doi.org/10.1080/23311916.2018.1446667.

[28] P. Parnian, A. D'Amore, Fabrication of high-performance CNT reinforced polymer composite for additive manufacturing by phase inversion technique, Polymers 13 (22) (2021), https://doi.org/10.3390/polym13224007.

[29] N. Wei, Y. Tian, Y. Liao, N. Komatsu, W. Gao, A. Lyuleeva-Husemann, Q. Zhang, A. Hussain, E.X. Ding, F. Yao, J. Halme, K. Liu, J. Kono, H. Jiang, E.I. Kauppinen, Colours of single-wall carbon nanotubes, Adv. Mater. 33 (8) (2021), https://doi.org/10.1002/adma.202006395.

[30] K.S. Essien, G. Linassi, M. Larocque, A. Zucker-Levin, Incidence and Trends of Limb Amputation in First Nations and General Population in, 2021, pp. 2006–2019, https://doi.org/10.1371/journal.pone.0254543.

[31] E.E. Aleisa, R.A. Al-Jarallah, Triple bottom line evaluation of solid waste management strategies: a case study for an arid Gulf State, Kuwait, Int. J. Life Cycle Assess. 23 (1) (2018), https://doi.org/10.1007/s11367-1410-z.

[32] H.K. Breesam, Z.A. Kadhim Jawad, Application of the triple bottom line (TBL) concept to measure the maintenance performance of buildings, IOP Conf. Ser. Mater. Sci. Eng. 1090 (1) (2021), 012079, https://doi.org/10.1088/1757-899x/1090/1/012079.

[33] O. Okorie, M. Obi, J. Russell, F. Charnley, Review article: A triple bottom line examination of product cannibalization and remanufacturing: a review and research agenda, Sustain. Prod. Consum. 27 (2021) 958–974, https://doi.org/10.1016/j.spc.2021.02.013.

[34] M. Jahanshahi, A. Dehghani, Fabrication, Purification and Characterization of Carbon Nanotubes: Arc-Discharge in Liquid Media (ADLM), Synth. Appl. CNT Their Compos. (2013), https://doi.org/10.5772/51116.

[35] N. Berrada, A. Desforges, C. Bellouard, E. Flahaut, J. Gleize, J. Ghanbaja, B. Vigolo, Protecting carbon nanotubes from oxidation for selective carbon impurity elimination, J. Phys. Chem. C 123 (23) (2019) 14725–14733, https://doi.org/10.1021/acs.jpcc.8b12554.

[36] A.F. Ismail, P.S. Goh, J.C. Tee, S.M. Sanip, A review of purification techniques for carbon nanotubes, Nano: Brief Rep. & Rev. 3 (3) (2008) 127–134.

[37] K.O. Yoro, M.O. Daramola, P.T. Sekoai, U.N. Wilson, O. Eterigho-Ikelegbe, Update on current approaches, challenges, and prospects of modeling and simulation in renewable and sustainable energy systems, Renew. Sustain. Energy Rev. 150 (2021), 111506, https://doi.org/10.1016/j.rser.2021.111506.

[38] S.A. Rouf, Z. Usman, H.T. Masood, A.M. Majeed, M. Sarwar, W. Abbas, Synthesis and Purification of Carbon Nanotubes, Carbon Nanotubes - Redefining the World of Electronics, 2021, https://doi.org/10.5772/intechopen.98221 [Online]. Available:.

[39] T.Q. Tran, R.J. Headrick, E.A. Bengio, S.M. Myint, H. Hamed Khoshnevis, V. Jamali, H.M. Duong, M. Pasquali, Purification and dissolution of carbon nanotube fibers spun from floating catalyst method, ACS Appl. Mater. Interfaces (2017) 1–8, https://doi.org/10.1021/acsami.7b09287.

[40] Z. Aws, A. Ghaleb, M. Jaafar, A.A. Rashid, Fabrication Methods of Carbon-Based Rubber Nanocomposites and Their Applications, Carbon-Based Nanofillers and Their Rubber Nanocomposites, 2019, https://doi.org/10.1016/B978-0-12-817342-8.00003-2.

[41] B. Mensah, H.G. Kim, J.H. Lee, S. Arepalli, C. Nah, Carbon nanotube-reinforced elastomeric nanocomposites: a review, Int. J. Smart & Nano Mater. 6 (4) (2015) 211–238, https://doi.org/10.1080/19475411.2015.1121632.

[42] J.M. Wernik, S.A. Meguid, Recent development in multifunctional nanocomposites using carbon nanotubes, Appl. Mech. Rev. 63 (2011) 1–40.

[43] M.H. Rashid, S.F. Ralph, Carbon nanotube membrane: synthesis, properties, and future filtration applications, Nanocompos 7 (99) (2017) 1–28, https://doi.org/10.3390/nano7050099.

[44] M. Bhattacharya, Polymer nanocomposites – a comparison between carbon nanotubes, graphene, and clay as nanofillers, Materials 9 (2016) 262.

[45] T.J. Simmons, J. Bult, D.P. Hashim, R.J. Linhardt, P.M. Ajayan, Non-covalent functionalization as an alternative to oxidative, acid treatment of single wall carbon nanotubes with applications for polymer nanocomposites, ACS Nanotechnol 3 (4) (2009) 865–870.

[46] Z. Syrgiannis, M. Melchionna, M. Prato, Encyclopedia of polymeric nanomaterials, Encyclopedia of Polymeric Nanomater 1 (2020) 1–8, https://doi.org/10.1007/978-3-642-36199-9.

[47] P. Sharma, P. Negi, N. Mahindroo, Recent advances in polymeric drug delivery carrier systems, Adv. in Polym. for Biomed. Applications (2018) 369–388.

[48] S. Kappenthuler, S. Seeger, Assessing the long-term potential of fiber reinforced polymer composites for sustainable marine construction, J. Ocean Eng. Marine Energ. 7 (2) (2021) 129–144, https://doi.org/10.1007/s40722-021-00187-x.

[49] K.L. Pickering, M.G. Arnan Efendy, T.M. Le, A review of the recent development in natural fibre composites and their mechanical performance, Compos. Appl. Sci. Manuf. 83 (2016) 98–112, https://doi.org/10.1016/j/composites.A.2015.08.038.

[50] S. Kumar, L. Prasad, V.K. Patel, V. Kumar, A. Kumar, A. Yadav, J. Winczek, Physical and mechanical properties of natural leaf fibre-reinforced epoxy polyester composites, Polymers 13 (9) (2021), https://doi.org/10.3390/polym13091369.

[51] M. Ravi, R.R. Dubey, A. Shome, S. Guha, C. Anil Kumar, Effect of surface treatment on Natural fibers composite, IOP Conf. Ser. Mater. Sci. Eng. 376 (1) (2018), https://doi.org/10.1088/1757-899X/376/1/012053.

[52] M.A. Zwawi, Review on natural fiber bio-composites, surface modifications and applications, Molecules 26 (2) (2021), https://doi.org/10.3390/molecules26020404.

[53] M. Latif, M.N. Prabhakar, J. Song, Fabrication of hybrid matrix/silane modified carbon fabric composites and study of their mechanical properties, J. Appl. Polym. Sci. 136 (2019), 47695, 10.1002.app.47695.

[54] M. Ramesh, Progress in Materials Science Flax (Linum usitatissimum L) fibre reinforced polymer composite materials: a review on preparation, properties, and prospects, Prog. Mater. Sci. 102 (2019) 109–166, https://doi.org/10.1016/j.pmatsci.2018.12.004.

[55] A. Atmakuri, A. Palevicius, A. Vilkauskas, G. Janusas, Review of hybrid fiber based composites with nano particles, Mater. Prop. Appl. 12 (2020) 2088, https://doi.org/10.3390/polym12092088.

[56] M.A. AlMaadeed, R. Kahraman, P.N. Khanam, N. Madi, Date palm wood flour/glass fibre reinforced hybrid composites of recycled polypropylene Mechanical and thermal properties, Mater. Des. 42 (2012) 289–294.

[57] P. Sivaranjana, V.A. Arumugaprabu, A brief review on mechanical and thermal properties of banana fibre-based hybrid composites, SN Appl. Sci. 3 (2) (2021) 1–8, https://doi.org/10.1007/s42452-021-04216-0.

[58] R. Soundararaj, K. Senthilvel, N. Rathinam, B. Prabu, Experimental studies on mechanical properties of natural rubber carbon black-carbon nanotube composite, Mater. Today Proc. 38 (2020) 3077–3084, https://doi.org/10.1016/j.matpr.2020.09.479.

[59] H. Yang, L. Yuan, X. Yao, Z. Zheng, D. Fang, Monotonic strain sensing behavior of self-assembled carbon nanotubes/graphene silicone rubber composites under cyclic loading, Compos. Sci. Technol. 200 (2020), 108474, https://doi.org/10.1016/j.compscitech.2020.108474.

[60] Y. Li, G. Liu, L. Wang, J. Zhang, M. Xu, S.Q. Shi, Multifunctional conductive graphite/cellulosic microfiber-natural rubber composite sponge with ultrasensitive collision-warning and fire-waring, Chem. Eng. J. 431 (2022), https://doi.org/10.1016/j.cej.2021.134046.

[61] R. Selvaraj, M. Ramamoorthy, A.B. Arumugam, Experimental and numerical studies on the dynamic performance of the rotating composite sandwich panel with CNT reinforced MR elastomer core, Compos. Struct. 277 (2021), https://doi.org/10.1016/j.compstruct.2021.114560.

[62] H. Guo, S. Jerrams, Z. Xu, Y. Zhou, L. Jiang, L. Zhang, L. Liu, S. Wen, Enhanced fatigue and durability of carbon black/natural rubber composites reinforced with graphene oxide and carbon nanotubes, Eng. Fract. Mech. (2020) 223, https://doi.org/10.1016/j.engfracmech.2019.106764.

[63] J.S. Gao, Z. Liu, Z. Yan, Y. He, A novel slurry blending method for uniform dispersion of carbon nanotubes in natural rubber composites, Results Phys. (2019) 15, https://doi.org/10.1016/j.rinp.2019.102720.

[64] D. Veeman, M.V. Shree, P. Sureshkumar, T. Jagadeesha, L. Natrayan, M. Ravichandran, P. Paramasivam, Sustainable development of carbon nanocomposites: synthesis and classification for environmental remediation, J. Nanomater. (2021), https://doi.org/10.1155/2021/5840645.

[65] Y. Zhan, S. Hao, Y. Li, C. Santillo, C. Zhang, L. Sorrentino, M. Lavorgna, H. Xia, Z. Chen, High sensitivity of multi-sensing materials based on reduced graphene oxide and natural rubber: the synergy between filler segregation and macro-porous morphology, Compos. Sci. Technol. (2021) 205, https://doi.org/10.1016/j.compscitech.2021.108689.

[66] S.S. Banerjee, L. Arief, R. Berthold, M. Wiese, M. Bartholdt, D. Ganguli, S. Mitra, S. Mandal, J. Wallaschek, A. Raatz, G. Heinrich, A. Das, Super-elastic ultrasoft natural rubber-based piezoresistive sensors for active sensing interface embedded on a soft robotic actuator, Appl. Mater. Today 25 (2021), https://doi.org/10.1016/j.apmt.2021.101219.

[67] J.K. Oleiwi, Q.A. Hamad, S.A. Abdulrahman, Flexural, impact and max. shear stress properties of fibers composite for the prosthetic socket, Mater. Today Proc. (2022), https://doi.org/10.1016/j.matpr.2021.12.368.

[68] J.L. Lin, S.M. Su, Y.B. He, F.Y. Kang, Improving the thermal and mechanical properties of an alumina-filled silicone rubber composite by incorporating carbon nanotubes, Xinxing Tan Cailiao/New Carbon Mater. 35 (1) (2020), https://doi.org/10.1016/S1872-5805(20)60476-0.

[69] P. Jawahar, V. Payak, J. Chandradass, P. Prabhu, Optimization of mechanical properties of CNT-rubber nanocomposites, Mater. Today Proc. 45 (2020) 7183–7189, https://doi.org/10.1016/j.matpr.2021.02.413.

[70] P. Bernal-Ortega, M.M. Bernal, A. Gonz, P. Posadas, R. Navarro, J.L. Valentín, New Insight into Structure-Property Relationships of Natural Rubber and Styrene-Butadiene Rubber Nanocomposites Filled with MWCNT, 2020, p. 201, https://doi.org/10.1016/j.polymer.2020.122604.

[71] T.N. Lam, G.S. Lee, B. Kim, H. Dinh Xuan, D. Kim, S.I. Yoo, J. Yoon, Microfluidic preparation of highly stretchable natural rubber microfiber containing CNT/PEDOT: PSS hybrid for fabric-sewable wearable strain sensor, Compos. Sci. Technol. 210 (2021), https://doi.org/10.1016/j.compscitech.2021.108811.

[72] J. Jose, S. Athikalam Paulose, Studies on natural rubber nanocomposites by incorporating zinc oxide modified graphene oxide, J. Rubber Res. 23 (4) (2020) 311–321, https://doi.org/10.1007/s42464-020-00059-3.

[73] H. Sun, T. Ji, H. Bi, M. Xu, L. Cai, M. Manzo, Synergistic effect of carbon nanotubes and wood-derived carbon scaffold on natural rubber-based high-performance thermally conductive composites, Compos. Sci. Technol. 213 (2021), https://doi.org/10.1016/j.compscitech.2021.108963.

[74] S. Lepak-Kuc, B. Podsiadły, A. Skalski, D. Janczak, M. Jakubowska, A. Lekawa-Raus, Highly conductive carbon nanotube-thermoplastic polyurethane nanocomposite for smart clothing applications and beyond, Nanomaterials 9 (9) (2019), https://doi.org/10.3390/nano9091287.

[75] C. Zhuang, R. Tao, X. Liu, L. Zhang, Y. Cui, Y. Liu, Z. Zhang, Enhanced thermal conductivity and mechanical properties of natural rubber-based composites co-incorporated with surface treated alumina and reduced graphene oxide, Diam. Relat. Mater. 116 (2021), https://doi.org/10.1016/j.diamond.2021.108438.

[76] N. Salah, A.M. Alfawzan, A. Saeed, A. Alshahrie, W. Allafi, Effective reinforcements for thermoplastics based on carbon nanotubes of oil fly ash, Sci. Rep. 9 (1) (2019), https://doi.org/10.1038/s41598-019-56777-1.

[77] W. Luan, Q. Wang, Q. Sun, Y. Lu, Preparation of CF/Ni-Fe/CNT/silicone layered rubber for aircraft sealing and electromagnetic interference shielding applications, Chin. J. Aeronaut. 34 (10) (2021) 91–102, https://doi.org/10.1016/j.cja.2020.12.040.

[78] N. Bumbudsanpharoke, S. Ko, Nanoclays in food and beverage packaging, J. Nanomater. (2019), https://doi.org/10.1155/2019/8927167.

[79] S. Lai, G. Guo, Two-way shape memory effects of sulphur vulcanized natural rubber (NR) and NR/paraffin wax (PW)/carbon nanotube nanocomposites, Polym. Test. 77 (2019), 105892, https://doi.org/10.1016/j.polymertesting.2019.05.008.

[80] F. Gariboldi, D. Pasquarelli, A.G. Cutti, Structural testing of lower-limb prosthetic sockets: a systematic review, Med. Eng. Phys. 99 (2022), https://doi.org/10.1016/j.medengphy.2021.103742.

[81] M.S. Scholz, J.P. Blanchfield, L.D. Bloom, B.H. Coburn, M. Elkington, J.D. Fuller, M.E. Gilbert, S.A. Muflahi, M.F. Pernice, S.I. Rae, J.A. Trevarthen, S.C. White, P.M. Weaver, I.P. Bond, The use of composite materials in modern orthopedic medicine and prosthetic devices: a review, Compos. Sci. Technol. 71 (16) (2011) 1791–1803, https://doi.org/10.1016/j.compscitech.2011.08.017.

[82] S. Shah, B. Gashi, S. Hoque, M. Marian, A. Rosenkranz, Enhancing mechanical and biomedical properties of prostheses - surface and material design, Surface. Interfac. 27 (2021), https://doi.org/10.1016/j.surfin.2021.101498.

[83] O. Eterigho-Ikelegbe, K.O. Yoro, S. Bada, Coal as a filler in polymer composites: a review, Resour. Conserv. Recycl. 174 (2021) 105756, https://doi.org/10.1016/j.resconrec.2021.105756.

[84] S. Abazari, A. Shamsipur, H.R. Bakhsheshi-Rad, A.F. Ismail, S. Sharif, M. Razzaghi, S. Ramakrishna, F. Berto, Carbon nanotubes (CNTs)-reinforced magnesium-based matrix composites: a comprehensive review, Materials 13 (19) (2020) 1–38, https://doi.org/10.3390/ma13194421.

[85] A.K. Ghosh, M. Dwivedi, Advantages and applications of polymeric composites, in: Processability of Polymeric Composites, Springer, 2020, https://doi.org/10.1007/978-81-322-3933-8_2.

[86] S. Bal, S.S. Samal, Carbon nanotube reinforced polymer composites - a state of the art, Bull. Mater. Sci. 30 (4) (2007), https://doi.org/10.1007/s12034-007-0061-2.

[87] T.R. Pozegic, J.V. Anguita, I. Hamerton, K.D.G.I. Jayawardena, J.S. Chen, V. Stolojan, P. Ballocchi, R. Walsh, S.R.P. Silva, Multi-functional carbon fibre composites using carbon nanotubes as an alternative to polymer sizing, Sci. Rep. 6 (2016), https://doi.org/10.1038/srep37334.

[88] E.G. Barathi Dassan, A. Anjang Ab Rahman, M.S.Z. Abidin, H.M. Akil, Carbon nanotube-reinforced polymer composite for electromagnetic interference application: a review, Nanotechnol. Rev. 9 (1) (2020) 768–788, https://doi.org/10.1515/ntrev-2020-0064.

[89] B. Salahuddin, S.N. Faisal, T.A. Baigh, M.N. Alghamdi, M.S. Islam, B. Song, X. Zhang, S. Gao, S. Aziz, Carbonaceous materials coated carbon fiber reinforced polymer matrix composites, Polymers 13 (16) (2021), https://doi.org/10.3390/polym13162771.

[90] B. Oldfrey, A. Tchorzewska, R. Jackson, M. Croysdale, R. Loureiro, C. Holloway, M. Miodownik, Additive manufacturing techniques for smart prosthetic liners, Med. Eng. Phys. 87 (2021) 45–55, https://doi.org/10.1016/j.medengphy.2020.11.006.

[91] H.R. Interaction, L. Chen, X. Guo, Y. Luo, Z. Jia, Y. Chen Inorganic and Organic Hybrid Nanoparticles as Multifunctional Crosslinkers for Rubber, (n.d.), 10.3390/polym10101138.

[92] Y. Li, G. Liu, L. Wang, J. Zhang, M. Xu, S.Q. Shi, Multifunctional conductive graphite/cellulosic microfiber-natural rubber composite sponge with ultra-sensitive collision-warning and fire-waring, Chem. Eng. J. 431 (2022), https://doi.org/10.1016/j.cej.2021.134046.

[93] J.O. Oboh, J.O. Okafor, A.S. Kovo, A.S. Abdulrahman, Dynamic mechanical properties of crosslinked natural rubber composites reinforced with cellulosic nanoparticles, Nig. J. Technol. 37 (3) (2018) 668–673, https://doi.org/10.4314/njt.v37i3.16.

[94] M. Hemmat Esfe, A. Esfa, A new generation of hybrid-nanofluid: thermal properties enriched lubricant fluids with controlled viscosity amount, SN Appl. Sci. 2 (7) (2020) 1–16, https://doi.org/10.1007/s42452-020-2875-0.

[95] A.N. Hadi, J.K. Oleiwi, Improve flexural strength of PMMA/SR polymer blend by reinforcement with carbon fiber as prosthetic foot material, Int. J. Appl. Innov. Eng. Manag. 4 (2) (2015) 172–176.

[96] A.N. Hadi, J.K. Oleiwi, Improving tensile strength of polymer blends of prosthetic foot material reinforcement by carbon fibre, J. Mater. Sci. Eng. 4 (2) (2015) 1–3, https://doi.org/10.4172/2169-0022.1000158.

[97] Y.S. Park, M. Huh, S.J. Kang, S. Yun, K.H. Ahn, Effect of CNT diameter on physical properties of styrene butadiene rubber nanocomposites, Carbohydr. Lett. 10 (4) (2009) 320–324.

[98] X. Zhou, Y. Zhu, J. Liang, S. Yu, New fabrication and mechanical properties of styrene butadiene rubber/carbon nanotubes nanocomposites, J. Sci. Technol. 26 (12) (2010) 1127–1132.

[99] J.C. Kearns, R.L. Shambaugh, Polypropylene fibers reinforced with carbon nanotubes, J. Appl. Polym. Sci. 86 (8) (2002) 2079–2084.

[100] F. Hussain, M. Hojjati, M. Okamoto, R.E. Gorga, Review article: polymer matrix nanocomposites, processing, manufacturing, and application: an overview, J. Compos. Mater. 40 (17) (2006) 1511–1575, 10.1177.00219983060-67321.

[101] Y.K. Chakravarthy, D. Suneel, D. Lingaraju, Alternate material for modeling and analysis of prosthetic knee joint, Int. J. Sci. Adv. Technol. 1 (5) (2011) 262–266.

[102] M.A. Muter, Q.K. Mugar, The study of the development of natural rubber blends using different types of polymers and fillers on the mechanical and chemical properties of the vulcanizates, J. Nat. Sci. Res. 4 (24) (2014) 60–73.

[103] S. Sagar, N. Iqbal, A. Maqsood, M. Bassyyouni, MWCNTs incorporated natural rubber composites: thermal insulation, phase transition, and mechanical properties, IACSIT Int. J. Eng. Technol. 6 (3) (2014) 168–173.

[104] M. Frigione, M. Lettieri, Durability issues and challenges for material advancements in FRP employed in the construction industry, Polymers 10 (3) (2018), https://doi.org/10.3390/polym10030347.

[105] J. Prasek, J. Drbohlavova, J. Chomoucka, J. Hubalek, O. Jasek, V. Adam, R. Kizek, Methods for carbon nanotubes synthesis – Review, J. Mater. Chem. 21 (40) (2011) 5872–15884.

[106] M. Pitkin, What can normal gait biomechanics teach a designer of lower limb prostheses? Acta Bioeng. Biomech. 15 (1) (2013) 3–10.

[107] S. Akhtar, M. Saad, P. Pandey, Overview of current advances in the development of polymer composite in biomedical applications, Mater. Today Proc. 5 (2018), in: www.sciencedirect.comwww.materialstoday.com/proceedings2214-7853.

[108] D. Maiti, X. Tong, X. Mou, K. Yang, Carbon-based nanomaterials for biomedical applications: a recent study, Frontiers 9 (2019) 1–16, https://doi.org/10.3389/fphar.2018.01401.

[109] A.S. Sethulekshmi, A. Saritha, K. Joseph, A comprehensive review of the recent advancements in natural rubber nanocomposites, Int. J. Biol. Macromol. 194 (2022) 819–842, https://doi.org/10.1016/j.ijbiomac.2021.11.134.

[110] L. Aryasomayajula, K.J. Wolter, Carbon nanotube composites for electronic packaging applications: a review, J. Nanotechnol. (2013), https://doi.org/10.1155/2013/296517.

[111] S. Zhang, J. Pang, Y. Li, F. Yang, T. Gemming, K. Wang, X. Wang, S. Peng, X. Liu, B. Chang, H. Liu, W. Zhou, G. Cuniberti, M.H. Rümmeli, Emerging internet of things driven carbon nanotubes-based devices, Nano Res. 15 (5) (2022) 4613–4637, https://doi.org/10.1007/s12274-021-3986-7.

[112] J. Simon, E. Flahaut, M. Golzio, Overview of carbon nanotubes for biomedical applications, Materials 12 (4) (2019) 624, https://doi.org/10.3390/ma12040624.

[113] M. Hussain, S. Yasin, H. Memon, Z. Li, X. Fan, M.A. Akram, W. Wang, Y. Song, Q. Zheng, Rheological and mechanical properties of silica/nitrile butadiene rubber vulcanizates with eco-friendly ionic liquid, Polymers 12 (2020) 2763, https://doi.org/10.3390/polym12112763.

[114] A.N. Amsan, A.K. Nasution, M.H. Ramlee, A short review on the cost, design, materials, and challenges of the prosthetics leg development and usage, Int. Conf. CELSciTech (2019), https://doi.org/10.2991/iccelst-st-19.2019.12.

[115] P. Huntjens, R. Kemp, The importance of a natural social contract and Co-evolutionary governance for sustainability transitions, Sustainability 14 (5) (2021) 1–26.