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REVIEW

A review on recent researches on polylactic acid/carbon nanotube composites

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Abstract As multifunctional high-performance materials, polylactic acid/carbon nanotube (PLA/CNT) composites are currently of great interest for using in an extensive range of medical and industrial applications. The main focus of the present work, accordingly, is to review the recent developments on PLA/CNT composites. In addition, the dependence of thermal, mechanical, electrical, and rheological properties on the type, aspect ratio, loading, dispersion state, and alignment of CNTs within PLA matrix was reviewed. The discussion of the different properties revealed that the CNTs additive could be an effective method to improve the performance of PLA materials for medical and industrial applications.

Keywords Polylactic acid · Carbon nanotube · Dispersion · Thermal properties · Mechanical properties

Introduction

Biodegradable materials based on polylactic acid (PLA), wood, thermoplastic starch, and other materials have been widely investigated toward their potential for industrial applications [1–4]. Among them, PLA derived from renewable resources, such as corn and sugar, has attracted considerable attention as a candidate for substituting polymers [5]. However, its relatively poor mechanical properties, slow crystallization rate, and low heat resistance limit its use in a wide-range of

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applications [6, 7]. Therefore, several modifications have been suggested to overcome the aforementioned problems, such as copolymerization [8], polymer blending [9], and incorporation of additives into PLA matrix [10]. Among them, the incorporation of additives, such as such as clay, graphene, and carbon nanotubes (CNTs) was regarded as a useful and effective way to control the rate of crystallization as well as to improve mechanical and electrical properties of PLA [11].

Due to their excellent mechanical, electrical, and magnetic properties as well as their nanometer scale diameter and high aspect ratio, CNTs are promising additives [12]. In general, two types of CNTs; single-walled CNTs (SWCNTs) which consist of a single graphene layer rolled up into a seamless cylinder and multi-walled CNTs (MWCNTs) which consist of multiple concentric cylinders were available. Irrespective of the type of CNTs, nanostructured polymeric composites based on CNTs have been the subject of intense investigations [13–15]. For instance, in terms of biodegradable polymer/CNTs composites, several studies showed that the incorporation of small amount of CNTs into the polymer matrix could significantly improve the performance of those composites [16, 17].

To the best our knowledge, only one review concentrated on of PLA/CNT composites where the influence of functionalized CNTs on the compatibility of PLA/CNT composites was highlighted [18]. However, there is lack of information regarding the material properties of PLA/CNT composites where the homogenous dispersion of CNTs with PLA matrix plays a crucial role in the fabrication of high-performance composites. Therefore, the main aim of this work was to outline the recent development in PLA/CNT composites.

Enhancement of dispersion of CNTs in PLA matrix

The performance of CNTs in PLA composites as a kind of reinforcement has not been fully achieved yet. Therefore, the uniform dispersion of CNTs within PLA matrix is of great importance for the preparation of high-performance PLA/CNT composites. Thus, there are several methods to improve the dispersion of CNTs in polymer matrix, such as solution mixing, melt mixing, in situ polymerization, and chemical functionalization [14].

Vicentini et al. [19] enhanced neurite out growth by obtaining a biocompatible porous scaffold using means of electrospinning a nanocomposite solution of poly(L-lactic acid) (PLLA) and 4-methoxyphenyl functionalized MWCNTs. The results revealed an improved adhesion and differentiation of cells growing onto CNT-PLLA. These results were explained by taking the role of CNT into account. First, CNTs not only led to low value of scaffold resistance in the bulk but also induced beneficial effects at the nanoscale. Second, CNTs could provide sites for cellular anchorage and guidance of cytoskeletal extensions thanks to their nanotopography.

In the study of Kong et al. [20], PLA/PCL-MWCNTs composites were fabricated by the electrospining technique, where MWCNTs were grafted first on PCL then mixed with PLA. They reported that PCL-MWCNT was embedded inside the fibers and the individual PCL-MWCNT was dispersed well in the fibers. Most of the

MWCNTs-PCL was well oriented along the axis of the electrospun fiber, which indicated that the functionalization on the surface of MWCNTs greatly improved the dispersion of nanotubes in the matrix solution.

Li et al. [21] successfully fabricated PLA/CNT composites with star PLA immobilized on the surface of CNTs using non-covalent method. The results indicated that CNTs are dispersed well in PLA matrix due the strong interactions in the supramolecular system.

An uniformly dispersion, orderly aligned of CNTs in PLA matrix through the strong shearing/stretching force during the melt spinning of PLA/CNTs composites containing 1 wt% CNT was established by Chen et al. [22]. The results summarized in Fig. 1 clearly revealed that the CNTs are completely separated and distributed uniformly in the whole fiber, parallel to each other at a separation distance of ~0.6 μm, as shown in Fig. 1a. In addition, it was found that the CNTs stretch and extend in the PLA matrix and well-organized alignment of CNTs might arise due to the rapid flow of PLA melts as well as considerable interactions at PLA/CNT interfaces (Fig. 1b). Chen et al. [23] prepared PLA/MWCNT composites by reacting MWCNT with PLA at various molecular weights. Thus, PLA was reacted with MWCNT functionalized with –COCl groups which was prepared by treating the purified MWCNT with HNO_3 followed by $SOCl_2$. The results indicated that the amount of grafted MWCNT increased from 46.5 to 53.1 wt% with increasing PLLA molecular weight from 1000 to 3000. Furthermore, the amount of grafted PLLA decreased when the molecular weight of the PLLA was further increased to 15,000.

Thermal properties

The thermal behavior of PLA/CNT composites could provide useful information that could be utilized to determine the optimum processing conditions and identify the potential applications of final products. Indeed, Seligra et al. [24] developed biodegradable composites with excellent bonding matrix-MWCNTs through the functionalization of the filler with modified PLA. They reported that the addition of

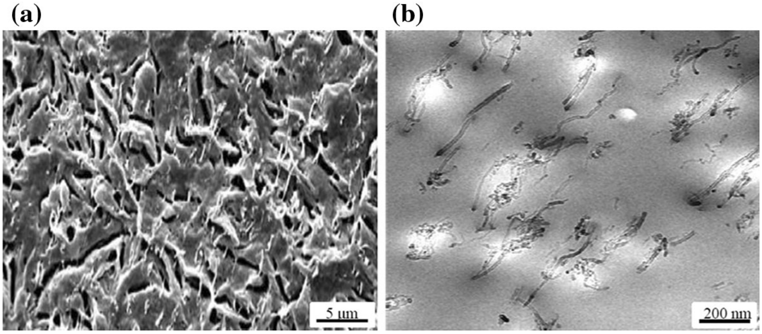

Fig. 1 **a** Scanning electron microscopy (SEM) image showing the CNTs aligned regularly on the surface, and **b** transmission electron microscopy (TEM) images showing the dispersion behavior of CNTs within PLA matrix [21]

MWCNTs in PLA-modified matrix could lead to shift the glass transition temperature (T_g), implying a very good adhesion between the modified PLA and the functionalized MWCNTs due to the higher surface area promoted by the incorporation of the MWCNTs.

Amirian et al. [25] investigated the effect of functionalized MWCNTs on the thermal stability of PLLA. The thermo-gravimetric analysis of the prepared composites with various concentrations of MWCNT-*g*-PLLAs showed a significant increment in the thermal stability of composites, by increasing the amount of MWCNT-*g*-PLLAs in composites. In addition, it was found that the MWCNT-*g*-PLLAs as heterogonous nucleation points led to increase the crystallinity of PLLA.

The isothermal melt crystallization behaviors of PLLA induced by both graphene and CNTs were examined [26]. It was found that the overall isothermal melt crystallization kinetics of PLLA could be accelerated by both graphene and CNTs which act as nucleating agents. As compared to graphene, additionally, it was found that the ability to accelerate crystallization induced by CNT was stronger than that induced by graphene.

The thermal properties was also enhanced using a "grafting onto" methods [27], where PLA-grafted MWCNTs are obtained by the reaction between acrylic acid-grafted PLA and hydroxyl-functionalized MWCNTs (MWCNTs-OH). The hydroxyl-functionalized CNTs were obtained by oxidation in the presence of a mixture between sulfuric acid and nitric acid, the formation of chloride acid-functionalized CNTs and its conversion into MWCNTs-OH with 1,6-hexanediol. The results listed in Table 1 revealed a dramatic enhancement in thermal properties of PLLA which was attributed to formation of ester groups through the reaction between carboxylic acid groups of PLA-*g*-acrylic acid and hydroxyl groups of MWCNTs-OH.

Shieh et al. [28] fabricated films of the PLLA/MWNTs-*g*-PLLA composites by a solution casting method to investigate the effects of the MWNTs-*g*-PLLA on the non-isothermal and isothermal melt crystallizations of the PLLA matrix. They reported that MWCNTs significantly improved the non-isothermal melt crystallization from the melt and the cold crystallization rates of PLLA on the subsequent heating.

Zhao et al. [29] investigated the effect of PLLA/carboxyl-functionalized MWCNT (f-MWCNT) on the thermal stability of PLLA/f-MWCNT composites. They reported that the hydrolytic degradation of PLLA could be enhanced after adding low contents of f-MWCNTs. This behavior was attributed to the fact that

Table 1 Glass transition (T_g) and melting temperatures (T_m) of PLA/CNT composites [26]

CNT content (wt%)	PLA/MWCNTs		PLA-grafted acrylic acid/MWCNTs	
	T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)
0	57.8	160.5	56.9	158.7
0.5	58.5	159.3	61.6	156.3
1	59.6	158.2	64.1	153.2
2	60.5	157.3	65.2	152.6
3	61.3	156.5	65.9	152.0

PLLA molecules in the composites might be attracted from alkaline solution easier than PLLA molecules in neat PLA. The hydrolytic degradation behavior of PLLA/CNT composites was also investigated by Chen et al. [30]. For this purpose, different contents of functionalized CNTs were introduced into PLLA and the composites were first annealed at different temperatures to obtain the semi-crystalline polymers with different degree of crystallinity. Then, the treated and untreated PLLA/CNTs composites were hydrolytically degraded. The results indicated that the presence of relatively high content of CNTs could improve the hydrolytic degradation ability of PLLA matrix. It is worth to mention that during the hydrolytic degradation process, the change of crystalline structure of PLLA matrix was mainly affected by two factors, such as initial amount of crystalline structure as well as the initial crystalline form of the PLLA matrix.

In the work of Fojt et al. [31], the effects of PLLA/MWCNT degradation products on human cells were reported. They suggested that secondary body reaction may appear after complete biodegradation of PLLA to lactic acid monomers in the presence of MWCNT.

In another study, Wu et al. [32] demonstrated that carboxylic-functionalized MWCNTs could act as nucleating agents on both the melt crystallization and the cold crystallization of PLA. In addition, the presence of CNTs could reduce the biodegradation rate of PLA which was attributed to the enhanced crystallinity degree of resulting PLA composites.

According to Kumar et al. [33], the crystallinity of the PLA matrix could affect the performance of sensing systems based on PLA/MWCNT composites. Although the content of MWCNTs and the preparation of sensing systems were different, they showed that the enhancement in crystallinity reduced the sensors performances in terms of sensitivity and selectivity.

Kim et al. [34] investigated the thermal degradation of PLLA/MWCNT and PLLA/PLLA-graft-MWCNT composites. They found that composites exhibited higher onset degradation temperature along with a higher amount of residue at the completion of degradation than neat PLLA. In addition, the activation energy calculated based on Kissinger were found to be 131.5 kJ/mol for PLLA, 143.7 kJ/mol for PLA/MWCNT, and 151.2 kJ/mol for PLLA/PLLA-*g*-MWCNT. Similarly, based on previous results reported by Kuan et al. [35] and Moon et al. [36], the degradation temperature of the PLLA/CNTs composites was higher than that of PLLA.

The crystallization behavior of PLA/MWCNT composites prepared by melt mixing method was investigated by Kim et al. [37]. They found that the crystallization temperature was shifted toward lower temperature ranges (84.5–100.6 °C) as incorporation of MWCNTs. The crystallization peak of pure PLA was disappeared in the first cooling of differential scanning calorimetry but that of PLA/MWCNT composites was evident which was related to nucleating effects of MWCNTs. According to Lizundia et al. [38], a significant enhancement of 100% on the thermal conductivity of PLA/CNT composites containing 3 vol% CNT was achieved. At contents up to 0.75 wt%, the thermal conductivity was reduced with the addition of CNT due to the presence of an interfacial resistance in which phonon scattering reduces the bulk thermal conductivity. With further addition of

CNT, a network of higher density of conducting pathways was achieved which led to increasing the thermal conductivity of the composites.

In the work of Zhao et al. [39], PLLA/carboxyl-functionalized MWCNT (f-MWCNTs) composites were prepared via solution mixing method to study the effect of f-MWCNT on the cold crystallization of PLLA. It was reported that the isothermal cold crystallization rate of neat PLLA and its composites increases with increasing crystallization temperature. In addition, the cold crystallization activation energy of PLLA was enhanced after composites preparation with f-MWCNTs and increase with increasing the f-MWCNTs contents, which was attributed to the physical hindrance effect of f-MWCNTs. Kong et al. [40] reported a decrease of the crystallization temperature of PLA induced by adding a small amount of MWNTs-PCL which led to the fact that heterogeneous nucleation effect which promoted crystallization of PLA, was rather obvious between MWNTs-PCL and PLA.

According to Park et al. [41], the incorporation of CNTs effectively enhanced the crystallization rate of the PLA matrix through heterogeneous nucleation, and a calorimetric characterization of the isothermal crystallization revealed that the crystallization kinetics of the PLA matrix were significantly increased in the presence of CNTs.

Finally, it is worth to mention that depending on the processing conditions, different crystal structures, such as α, α', β, and γ may be obtained for PLA [16]. The α' crystals would form at low crystallization temperatures (<120 °C) during the melt crystallization whereas α crystals are more stable at elevated temperatures. The transformation from the α' to the α form could easily occur by heating at a certain temperature through solid–solid phase transition. On the other hand, polymorphic phases β and γ were hard to obtain [42]. According to Bautista et al. [42], the nanoparticles of silver could lead to fast crystallization and lower crystallization temperature of PLA/silver composites. A higher fraction of crystals changed from α' to α form upon the addition of silver nanoparticles modifying the lattice space of (200)/(110) peak corroborating the reorganization of crystals from α' to α. In terms of PLA/CNT composites, it was reported that the incorporation of 1 wt% of CNTs does not modify the crystalline structure of PLA and α- type was formed for PLA and PLA/CNT composites [16]. Such findings were consistent with previous results on other biodegradable polymer/CNT composites where the crystal type of poly(ethylene succinate) (PES) composites was not affected by the addition of CNTs [17].

Mechanical properties

Aligned-PLLA/PCL/functionalized MWCNT (f-MWCNT) composite fibrous membranes were fabricated by electrospinning [43]. It was reported that both tensile strength and Young's modulus of the composites increased with increasing content of the f-MWCNT. In addition, the composites containing 3.75 wt% f-MWCNT exhibited improvements of ~134% in tensile strength and ~102% in Young's modulus, indicating that the aligned f-MWCNT could lead to reinforce the electrospun PLLA/PCL blend fibrous membrances.

Also, Gupta et al. [44, 45] reported in vitro study that polylactic-*co*-glycolic acid/SWCNT composites are compatible which led to enhanced tensile strength compared with a pure polylactic-*co*-glycolic acid.

PLA/CNT composites with two different aspect of CNT via melt mixing method were fabricated by Wu et al. [46]. They demonstrated that the composites containing CNTs with high aspect ratio exhibited higher modulus than that with low aspect ratio at identical loading levels which was related to the microscopic dispersion of CNTs.

In the work of Kuan et al. [36], the surface-functionalization of CNTs in the presence of maleic anhydride (MA), followed by the coupling reaction with hydroxyl-functionalized PLA was investigated. The MA-MWCNT could lead to an increase of the interfacial bonding with the PLA matrix, resulting in a significant improvement in the mechanical properties of PLA.

Arenaza et al. [47] examined the addition of a non-covalent linker, the pyrene-end functionalized PLLA, (py-end-PLLA) on the mechanical properties of composites containing 0, 0.1, 0.5, and 1.0 wt% of MWCNT. In general, it was found that the Young's modulus increased while elongation decreased with the addition of MWCNTs. The Young's modulus of the PLLA/py-end-PLLA/MWCNT with 0.1 wt% of MWCNTs was 45% higher compared to the PLLA/py-end-PLLA control. On the other hand, the elongation at break tended to increase as py-end-PLLA was added, indicating that py-end-PLLA could act as a plasticizing agent for the high molecular weight PLLA matrix.

The effect of hybrid additive contains (clay-CNT) on the mechanical properties of PLA composites as a function of irradiation time was examined by Gorrasi et al. [48]. The results showed that the Young's modulus of pure PLA decreased linearly with an increase in irradiation time which was due to the chain cleavage UV inducted while the addition of additive could prevent the loss of mechanical consistence of PLA.

The mechanical properties of PLA/MWCNT-*g*-PLA composites were compared with PLA/MWCNT, PLA/carboxylic-functionalized MWCNTs composites [49]. The results revealed that tensile properties of PLA composites tended to be enhanced significantly in the PLA/MWCNT-*g*-PLA composites than those in PLA/MWCNT, PLA/carboxylic-functionalized MWCNTs composites. This behavior might be related to the good dispersity of MWCNTs in PLA/MWCNT-*g*-PLA which, in turn, was related to the enhanced compatibility of PLA chains in MWCNT-*g*-PLA with the neat PLA matrix.

According to Mat-Desa et al. [50], PLA/MWCNT composites containing of 5 phr of carboxylic-functionalized MWCNTs exhibited the highest tensile and flexural strengths where a uniform dispersion of MWCNTs was obtained in the matrix. On the other hand, the impact strength was decreased as the amount of MWCNTs increased.

Ramontja et al. [51] prepared PLA/fictionalized-MWCNTs composites using a twin-screw extruder. Mechanical results showed that both the tensile strength and elongation at break of PLA were improved with addition of functionalized-MWCNT, without a significant loss of modulus which was attributed the strong interactions in PLA-functionalized-MWCNT.

Amirian et al. [52] examined the effects of MWCNTs-*g*-PLLA on the mechanical properties of PLLA. Mechanical results showed that both ultimate tensile strength and elongation at break of PLLA/MWCNT-*g*-PLLAs composites were increased from 37.9 to 55.8 MPa and from 157 to 285%, respectively, in comparison to the neat PLLA. Chiu et al. [53] reported based on nano-indentation results that the both hardness and Young's modulus of PLA/CNT composites increased with increasing CNT content which was attributed to the good dispersion of CNTs in the PLA matrix. In addition, it was found that mechanical properties of the purified PLA/CNTs were better compared to the non-purified composites.

The effect of magnetic MWCNTs (m-MWCNTs) on the properties of PLA composites was investigated by Li et al. [54]. For this purpose, Fe_3O_4 nanoparticles are first decorated onto MWCNTs through Diels–Alder reaction. Then, m-MWCNTs were functionalized with PLA through an ozone-mediated process. The steps related to the preparation process of PLA/CNT composites are summarized in Fig. 2. Based on the mechanical results, it was found that Young's modulus and elongation at break of the composites containing 0.3 wt% m-MWCNTs were 25 MPa and 150%, respectively. According to Zhang et al. [55], the mechanical properties of the PLLA/SWCNT composites fabricated under a low draw ratio exhibited an insignificant change with addition of SWCNT while the composites fabricated under a high draw ratio showed significant increase in strength and elongation at break with addition of SWCNT, as shown in Fig. 3. This behavior was attributed to a possible stretching-induced formation of a brush-like hybrid structure in which the PLLA lamellae growing perpendicular to the SWCNTs axis for composites obtained at the high drown ratio.

Mina et al. [56] compared the mechanical properties of PLA mixed with treated and untreated of MWCNTs of different compositions via an extrusion process. MWCNT was treated using heat and acid treatments methods. For heat treatment, MWCNT was annealed at 1500 °C in a vacuum furnace and cooled to room

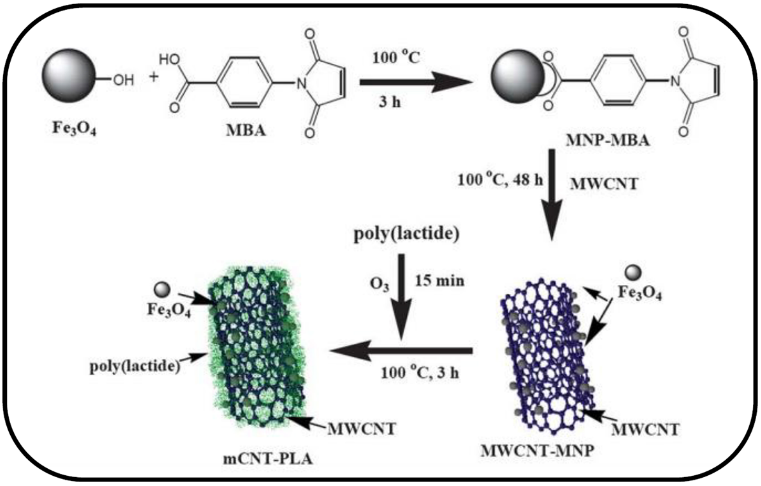

Fig. 2 Scheme shows steps of preparation of PLA/Fe_3O_4-MWCNT composites [53]

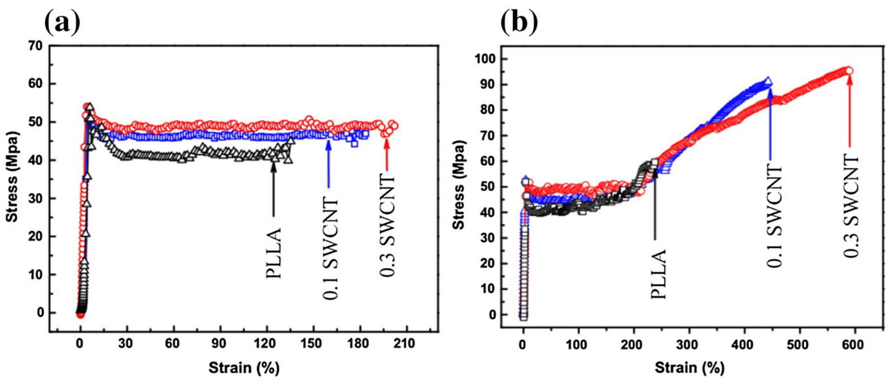

Fig. 3 Stress-strain curves of PLLA/SWCNTs composites at different contents of SWCNT prepared upon different ratio rate **a** low draw ration and **b** high draw ratio [54]

temperature. As for acid treatment, MWCNTs were dipped in HNO_3 solution for 8 h at 100 °C. The results showed that the composites containing 1 wt% MWCNTs subjected to acid treatment by HNO_3, exhibited a superior tensile strength and Young's modulus as compared to other samples.

Electrical properties

Electrical properties of PLA/CNT composites have been reported on in the literature. It has been found that CNTs are very effective in improving the electrical conductivity of these composite materials. According to Lin et al. [57], the electrical resistivity of PLA/MWCNT-*g*-PLA composites were found to increase from ∼ 104 to ∼ 1012 V/sq with increasing the PLA chain length of MWCNT-*g*-PLA. This result was attributed to the fact that the PLA chains grafted on MWCNTs could prevent the formation of the electrical conduction path of MWCNTs in the PLA matrix. In the work of Alam et al. [58], composites consisting of epoxidized soya oil plasticized- PLA and amine-functionalized carbon nanotubes (NH_2 functionalized- CNTs) were fabricated. It was reported that the composite with 5 wt% NH_2 functionalized CNTs exhibited optimum values of shape recovery. This behavior would be attributed to its relatively high electrical conductivity as well as an adequate degree of crosslinking between NH_2 functionalized CNTs and plasticized PLA matrix.

Lizundia et al. [59] characterized the PLLA/MWCNT composites prepared by solvent casting method. The results shown in Fig. 4 indicated that MWCNTs distributed randomly within the polymer matrix and a physical continuous pathway was formed at MWCNT concentrations of 0.25 and 0.5 wt%. Therefore, a percolation threshold was obtained within a range of 0.21–0.33 wt% MWCNTs, and the conductivity was increased by six orders of magnitude (Fig. 4b).

Li et al. [60] fabricated PLA/carboxyl-MWCNT via in situ polymerization method. The addition of carboxyl-MWCNT led to a significant improvement in the electrical conductivity of PLA. In another study, PLA/MWCNT composites with

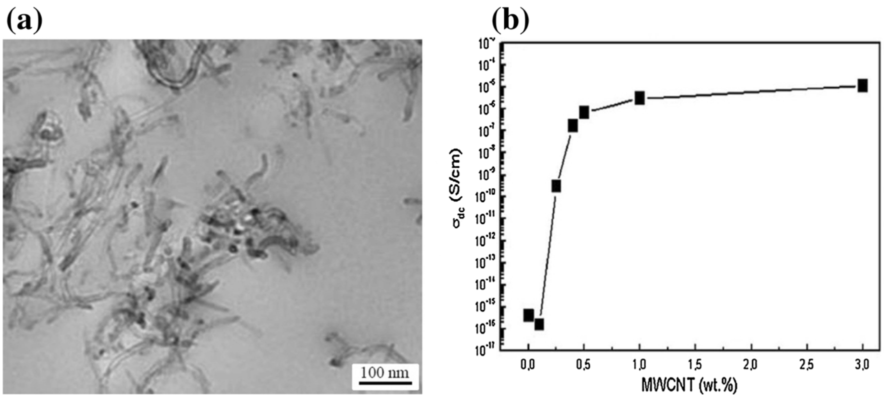

Fig. 4 **a** TEM image showing the dispersion behavior of MWCNT within PLLA matrix and **b** electrical conductivity of PLA/MWCNT composites with respect to MWCNT content [58]

different contents of MWCNTs (between 0.5 and 2.0 wt%) were fabricated via melt mixing process [61]. It was found that an electrical percolation threshold below 0.5 wt% MWCNT content was obtained which was related to the formation of a conductive network structure within the PLA matrix.

Yang et al. [62] investigated the electrospun PLA/CNTs composites and found that the morphology of obtained composites was closely related to the dispersion of CNTs in the fibers. Although CNTs could orient along the fiber axis, high loading levels of CNTs were dispersed as entangled bundles along the fiber axis. The addition of CNT less than 2 wt% could lead to a significant enhancement in the electrical conductivity.

Kim et al. [63] reported that the electrical resistivity of PLLA/MWCNTs decreased continuously with increasing MWCNT content compared to the counterpart containing PLLA-*g*-MWCNTs which was attributed to the fact that PLLA-*g*-MWCNTs prevented the direct connection between neighboring MWCNTs.

Antar et al. [64] reported that graphine/CNT hybrid fillers are an effective to improve the electrical conductivity of PLA up to 4123 S m^{-1}. Very recently, Sullivan et al. [65] fabricated PLA/CNT composites using two methods. First, melt mixing followed by melt fiber spinning. Second, solution mixing followed by electrospinning. They reported that the solution mixing method and electrospun fibers resulted in a higher conductance compared to the PLA/CNT films of the same CNT content made by melt compounding due to a more heterogeneous distribution and dispersion of CNT throughout.

Rheological properties

Park et al. [41] reported that PLA/CNT composites exhibited a non-Newtonian behavior where the complex viscosity was decreased with increasing frequency. The results of this works are summarized in Fig. 5. At lower frequencies, the

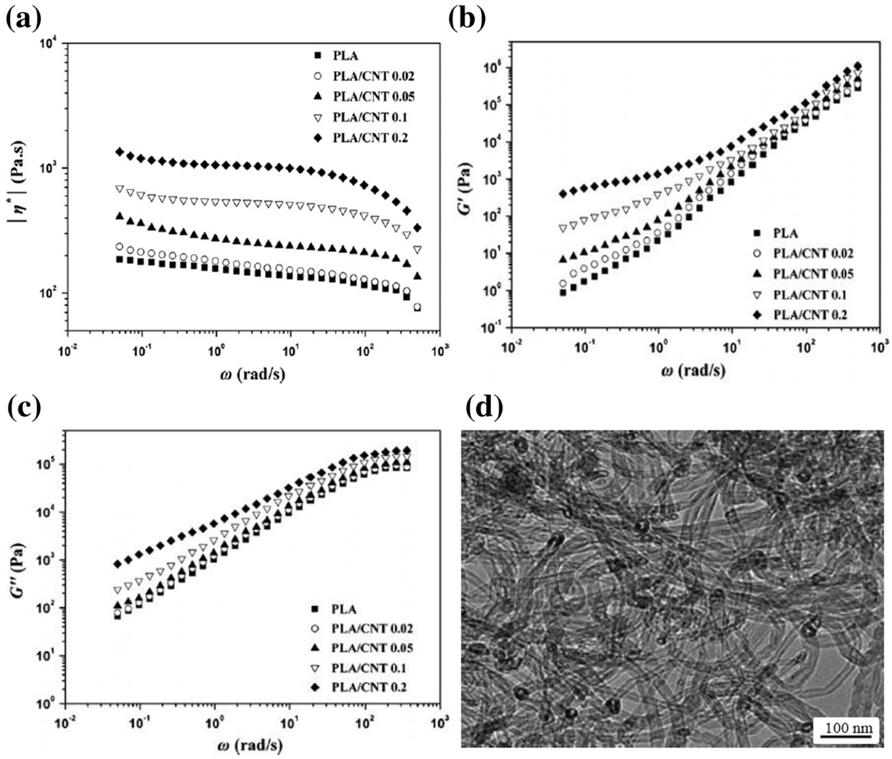

Fig. 5 **a** Complex viscosities of the PLA/CNT composites at 190 °C with respect to frequency, variation of **b** storage and **c** loss moduli of the PLA/CNT composites with CNT content as a function of frequency, respectively, and **d** TEM image showing PLA/CNT composites with a CNT content of 0.02 wt% [41]

interconnected structures resulted from CNT–CNT and CNT–PLA matrix interactions led to a more significant effect of the CNTs on the complex viscosities of the composites compared with high frequencies (Fig. 5a). The gradient of a plot of log G' versus log G'' (where G' and G'' are the storage and loss moduli) of the PLA/CNT composites decreased with increasing CNT content, indicating an increase in heterogeneity as shown in Fig. 5b–d.

The effect of various functionalized MWCNTs, such as carboxylic-MWCNT and hydroxyl-MWCNT as well as purified MWCNTs on the rheological properties PLA/CNT composites was investigated by Wu et al. [66]. It was found that PLA/carboxylic-MWCNTs composites showed a typical solid-like viscoelastic response at low frequencies under small amplitude oscillatory shear flow and the percolation threshold was lower than 3 wt%. Furthermore, the presence of carboxylic-functionalized MWCNTs led lo the better dispersion in the PLA matrix than the hydroxyl and purified MWCNTs since the corresponding composites exhibited the lowest rheological percolation threshold.

According to Xu et al. [67], functionalized MWCNTs (f-MWCNT) were successfully prepared by covalent grafting reactions between five-arm PLA and acyl-chloride-functionalized MWCNT. Rheological results indicated that addition of f-MWCNTs in PLA matrix has a dramatic influence on the low frequency relaxations of PLA chains. In addition, a percolated network structure was formed at about 2.0 wt% f-MWNTs content.

Other properties

The effects of MWCNTs on the photo oxidation stabilization of PLA/MWCNT composites were studied by Gorrasi and Sorrentino [68]. For this purpose, the composites were exposed to UV irradiation (220–640 nm) with irradiation intensity of 125 W/m^2 at a constant temperature of 30 °C and constant relative humidity of 50% for several days. It was found that the rate of photo-degradation of PLA/MWCNT composites was lower than that of the pure PLA (Fig. 6). This result indicated that MWCNTs could prevent the transport of decomposition products in PLA matrix and retarded the evolution of the degradation process.

Krul et al. [69] examined the effect of MWCNT on the stability of PLA to thermal oxidative destruction and found that the addition of MWCNT into PLA led to enhance the stability of PLA to thermal oxidative destruction, expecting that implants from PLA/MWCNTs composites would be dispersed in a living organism more slowly as compared to the counterpart without MWCNTs.

In the work of Anaraki et al. [70], PLA/polyethylene glycol/MWCNT nanofibrous were prepared via electrospinning technique. Doxorubicin hydrochloride (DOX) as an anticancer drug was successfully encapsulated into these nanofibrous scaffolds. The results indicated that the cell viability of DOX-loaded nanofibers exhibited superior cytotoxic activities of DOX-loaded PLA/polyethylene glycol/MWCNT nanofibrous scaffolds.

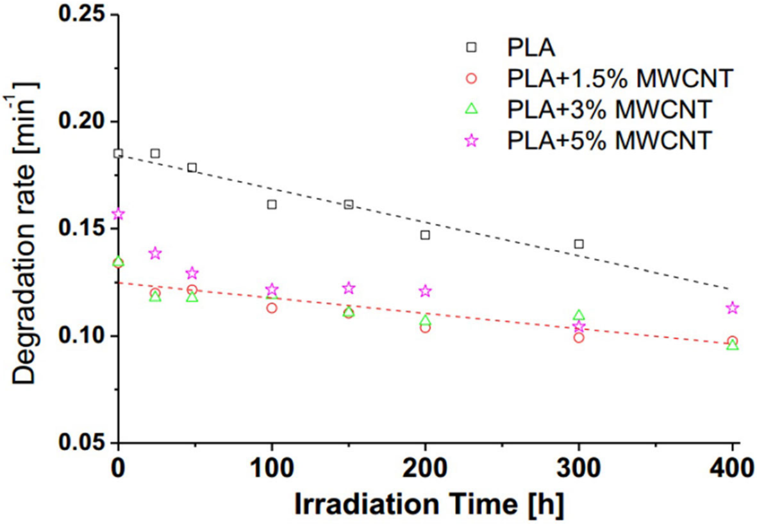

Fig. 6 Degradation rate of PLA/CNT with respect to UV irradiation time [67]

Recently, a facial solution mixing method was employed to prepare PLA/MWCNT composites followed by fabrication of vapor/gas sensing thin films [71]. The results revealed that the sensing elements fabricated from the PLA/MWCNTs composite materials exhibited good reproducibility and stability after multiple cycles. Mei et al. [72] successfully prepared an electrospun PLLA/MWCNT/hydroxyapatite composite fibrous membrane. They found that the membrane promoted the adhesion and proliferation of human periodontal ligament cells but inhibited those of gingival epithelial cells. In another study, Mai et al. [73] prepared degradation sensor based on PLA/CNT composites. They reported that PLA/CNT composites demonstrated excellent degradation sensing abilities at CNT contents around the percolation threshold, with resistivity changes of about four orders of magnitude with biodegradation.

Feng et al. [74] covalently grafted PLLA with magnetic-MWCNT (m-MWCNT) via in situ ring-opening polymerization of lactide. It was reported that m-MWCNTs-*g*-PLLA exhibited typical superparamagnetic performance and could be aligned under a lower magnetic field. According to Hapuarachchi and Peijs [75], the fire retardancy of PLA composites could be improved using MWCNT and sepiolite nano-clay as flame retardants. The results showed that the heat release capacity (HRC) which was an indicator of a materials fire hazard, decreased by 58% for the PLA ternary system based on sepiolite and MWCNTs. The improving flammability properties were explained by considering the differences in the condensed phase composition process into account. In addition, according to Bourbigot et al. [76], PLA/MWCNT composites prepared via reactive extrusion process exhibited a slight improvement of the flame retardancy. This behavior was attributed to formation of char layer covering the entire sample surface acting as an insulative barrier and reducing volatiles escaping to the flame for a certain period of time. However, this layer can be broken due to formation some cracks when burining.

In the study of Alam et al. [77], PLA was first plasticized by epoxidized linseed oil (ELO) to investigate its electroactive shape memory behavior. They found that the electroactive shape memory in the composites was significantly affected by the contents of CNT. Moreover, the composites containing 3 wt% MWCNTs exhibited a recovery of 95% within 45 s whereas the similar recovery level took 85 s when MWCNTs content was increased from 3 to 5 wt%.

A vivo biocompatibility of poly(lactic-*co*-glycolic acid) (PLAGA)/SWCNT composites for applications in bone and tissue regeneration was examined [78]. It was reported that both PLAGA and SWCNT/PLAGA showed a significantly higher sumtox score compared with the control group at all-time intervals. In addition, no difference in urinalysis, hematology, and absolute and relative organ weight was observed.

Applications

PLA/CNT composites are one of the most promising alternatives to polymer composites filled with conventional fillers. It was suggested that such composites can be used for biomedical applications, such as drug delivery systems, soft tissue engineering, and hard tissue engineering [11, 45]. In addition, the PLA/Fe_3O_4-MWCNT composites could be used as environmental-responsive materials and separation membranes [54]. According to [61], PLA/MWCNT composites are able to be adapted in sensors for liquid sensing. Also, PLA/CNT composites could be utilized as potential sensor materials for detection of some specific solvent vapors or gas pollutants in environmental protection [71].

Conclusion remarks

The reinforcement of PLA using CNTs nanoparticles has generated much scientific and commercial interest over the last two decades. However, significant advances are still needed to improve the dispersion of CNTs within PLA matrix to meet the requirements of most market applications. Several studies have shown that the addition of small amounts of CNT led to significant enhancements in thermal, mechanical, and electrical properties of PLA composites. The discussion of the different properties in this study indicated that the addition of CNT would be beneficial for improving the material performance of PLA composites for medical and industrial applications.

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