

Unzipped multiwalled carbon nanotubes-incorporated poly(L-lactide) nanocomposites with enhanced interface and hydrolytic degradation

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ABSTRACT

Much effort has been directed to the fabrication of polymer/multiwalled carbon nanotubes (MWCNTs) nanocomposites and the characterization of their physical properties. However, the enhancement of physical properties of nanocomposites has been greatly hampered by the limited available interface area of MWCNTs in nanocomposites. To overcome this intrinsic limitation, we investigated the nanocomposites of poly(L-lactide) (PLLA)/unzipped MWCNTs (μ CNTs), in which the μ CNTs were subjected to oxidative unzipping with different amounts of oxidant (KMnO_4). Besides the characterization of the μ CNTs, the crystallization of PLLA, the interface and the possible interaction between PLLA and μ CNTs were well characterized by several measurements including Fourier transform infrared (FT-IR) spectra, dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC), etc. As found, the interaction between PLLA and μ CNTs can be roughly tuned by controlling the oxidation degree of the MWCNTs. In this case, the ultimate values of the weight loss (a direct measure of the hydrolytic property) after 24 days exposure to NaOH solution can reach around 82.2 wt% for the PLLA/ μ CNT-5 nanocomposite, comparing to 41.8 wt% for neat PLLA. Additionally, the incorporation of μ CNTs was found to accelerate the hydrolytic degradation of PLLA in the nanocomposites.

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1. Introduction

During the last years, graphene nanosheets (GNSs) and graphene oxide nanosheets (GOSs), which are of quasi-1D nanostructure, have attracted widespread interest due to their unique structure, electronic properties, and promising applications in wide fields [1–3].

Structurally, both GOSs and carbon nanotubes (CNTs) are made up of graphite layers, indicating that they have the same fundamental structural unit. The most significant difference is their morphology: GOSs have a two-dimensional flat area made up of one- or several-atom layers, while the main tube part of CNTs can be regarded as consisting of curled graphite layers with two half-fullerenes capping two ends of the tube. Compared with the two-dimensional (2D) nanoplate-like GOSs, CNTs may be viewed as one-dimensional (1D) nanolines. More uniquely, GOSs behave as

a type of building block with hydrophobic π – π domains on the basal plane and hydrophilic carboxylic groups on the edge [4]. Therefore, GOSs exhibit an amphiphilic character and can be used as surfactants in numerous technological fields [5–7].

Very identical to the case of multiwalled carbon nanotubes (MWCNTs), however, tremendous difficulty has been encountered to realize the full potential of GNSs in improving the mechanical properties of polymers [8–10]. Some obstacles, such as poor dispersion and lack of interfacial bonding, which limit the reinforcement effect, have been partially addressed by either physical method (such as ultrasonication [11], high shear mixing [12], etc.) or chemical methods (covalent [13–15], or noncovalent modification [16,17] of the surface of MWCNT). It is demonstrated that controlling the dispersion of GNSs in polymer matrix and the interaction between them is the prerequisite to acquire the good reinforcement.

However, another important issue has always been overlooked. That is the available interface area (AIA) by which MWCNTs can interact with the matrix [18]. For MWCNT reinforced polymers, because only the outmost wall is exposed to the surrounding

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matrix, the AIA of MWCNT is almost 1 order of magnitude lower than single-walled carbon nanotubes (SWCNT) [19]. In other words, for MWCNT reinforced composites, only the outermost walls of MWCNTs could bear the stress and the inner walls could not efficiently participate in the stress transferring from the polymer matrix to the MWCNTs. This suppresses the reinforcement effect achievable in MWCNT/polymer nanocomposites [20]. Unfortunately, traditional strategies are only focused on surface functionalization to improve the interface action between MWCNTs and polymer matrix, and nearly no reports address this intrinsic limitation of MWCNTs as reinforced fillers.

Herein, we investigate a novel concept to increase effective surface of the MWCNTs in polymer nanocomposites by using unzipped MWCNTs (μ CNTs) as reinforced fillers [18]. Recently, various strategies have been reported for longitudinal unzipping of MWCNTs, such as oxidative unzipping [21,22] and electrical unwrapping [23]. The unzipped MWCNTs can be exfoliated into ribbonlike graphene layers in solution aided by sonication. In this study, the oxidative unzipping method was chosen to produce μ CNT for several reasons, such as cost-efficiency, readily tunable unzipping degree of CNTs, enhanced solvent dispersion, etc. Most importantly, the unzipping process can open and separate the walls of MWCNTs, which leads to the greatly increased AIA per volume MWCNTs and allow both the inner walls and the outermost walls to interact with the polymer matrix [19].

In this case, poly(L-lactide) (PLLA) was chosen as a model polymer for the following reasons. 1) PLLA is of special interest among the biopolymers. Structurally, PLLA is a type of polyester formed by condensation of L-lactic acid or ring-opening polymerization of the cyclic diester (L-lactide) [24]. Because of the presence of ester groups, it is susceptible to enzymatic and hydrolytic degradation to form L-lactic acid, a naturally occurring metabolite in the human body. 2) PLLA can have strong interactions with both pristine and oxidized CNT [25,26], and the process for the preparation of PLLA nanocomposites is simple and environmentally friendly. 3) PLLA will have a unique crystallization behavior influenced by the topological structure of a heterogeneous nucleating agent. In the presence of nanoclay, the intercalated and exfoliated PLLA-based nanocomposites exhibited a special crystallization kinetics and chain conformational changes during the crystallization process [27].

Many studies on PLLA-based nanocomposites have been performed to improve the properties of eco-friendly PLLA by incorporating nanoparticles such as clays and carbon nanotubes [28–30]. However, research on the hydrolytic-degradation behavior of PLLA-based nanocomposites containing graphene sheets or graphite nanoplatelets has been carried out limitedly [31].

2. Experimental section

2.1. Materials

MWCNTs (purity, 95%; length, ca. 10 μ m; and diameter, 30 nm) were obtained from Chengdu Organic Chemistry Co. PLLA (2002D, D-isomer content 4.3%, $M_w = 2.53 \times 10^5$ g mol⁻¹, melt flow rate (MFR) = 4–8 g/10 min (190 °C/2.16 kg), and density of 1.24 g cm⁻³) was purchased from Nature Works, USA. Concentrated sulfuric acid (95–98%), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂, 30%), and concentrated hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC), Beijing, and used as received.

2.2. Preparation of μ CNTs

μ CNTs were prepared by an oxidative unzipping method as originally reported by Kosynkin et al. [21]. First, 0.1 g of MWCNTs

was dispersed in 50 mL of concentrated sulfuric acid and stirred for 2 h until a visually homogeneous black solution formed. Then, different amounts of KMnO₄ (100, 200, 300, 400, and 500 wt% relative to the weight of MWCNTs) were slowly added to the solution and the solution was further stirred for 1 h at room temperature. After that, the temperature was gradually raised to 70 °C and maintained at that temperature for 1 h. Subsequently, the mixture was subject to the pulsed sonication for 1 h (2 s on and 1 s off) in an ice bath using a Vibra-Cell sonicator with a horn of 13 mm in diameter (JY-92IIN, 600 W, 50% amplitude). When the reaction was completed, the mixture was poured into 500 mL DI water with 3 mL H₂O₂. The solution was centrifuged and extensively washed with dilute hydrochloric acid (10%) six times and DI water three times prior to being dried in vacuum at 80 °C. These prepared μ CNTs via different amounts of KMnO₄ were denoted hereinafter as μ CNT-1, μ CNT-2, μ CNT-3, μ CNT-4, and μ CNT-5, respectively.

2.3. Fabrication of PLLA/CNT and PLLA/ μ CNTs nanocomposites

A typical procedure for the preparation of nanocomposites involved the dispersion of the required amount of μ CNT (3.75 mg) in 20 mL chloroform (CHCl₃), and sonication for 30 min to yield a homogeneous solution. Meanwhile, 0.75 g PLLA was dissolved in 10 mL CH₂Cl₂. Then, these two solutions were mixed together and sonicated for another 30 min. Finally, the PLLA/ μ CNTs solutions were poured onto a substrate and dried at 60 °C for 12 h. To completely remove the remnant solvent, the composite films were further dried in vacuum at 60 °C for 6 h. In this way, the PLLA/ μ CNTs nanocomposites with a constant mass ratio of 1000/5 (PLLA/ μ CNT, w/w) were fabricated.

2.4. Characterization

Fourier transform infrared (FT-IR) spectra were recorded on an IR Tensor 27, Bruker Corp. X-ray powder diffraction (XRD) spectra were recorded on a X'Pert X-ray diffraction spectrometer (Philips, USA) in reflection mode, using Cu K α radiation. Raman spectra were taken with Renishaw inVia-Raman Spectroscopy, equipped with a holographic grating of 1800 lines mm⁻¹ and a He–Ne laser (632.8 nm) as an excitation source. Specially adapted research grade 10X Leica microscope focused the excitation beam onto the samples. The data acquisition time used in the measurement was 20 s. Optical microscopy images of composite films were obtained using OM, E600POL, Nikon. The morphology of MWCNTs and μ CNTs was obtained using a scanning electron microscope (SEM) (Jeol 6490LV) and a transmission electron microscopy (TEM) (JEOL2100F). The degree of crystallinity of samples was measured by a differential scanning calorimeter (DSC), TA Q100 DSC, in a nitrogen flow (20 mL min⁻¹) with a heating rate of 10 °C min⁻¹, spanning the temperature range from 25 to 180 °C. To erase the possible thermal history, only the second DSC heating curves are collected. Thermogravimetric analysis (TGA) was performed in nitrogen with a Perkin–Elmer Diamond TA/TGA instrument at a heating rate of 20 °C min⁻¹. Dynamic mechanical analysis (DMA) was performed on the rectangular samples of 42 mm $\times$ 8 mm $\times$ 1 mm in size using a dynamic mechanical analyzer Q800 from TA Instruments under tension film mode span a temperature range of 20–150 °C at a frequency of 1 Hz and a heating rate of 3 °C min⁻¹.

The hydrolytic degradation of neat PLLA and its nanocomposites was conducted in sodium hydroxide (NaOH) solution (pH = 13) at 37 °C [32]. The degradation was determined by the weight loss as a function of time. The weight loss coefficient W_{loss} (wt%) was evaluated by the following relationship: $W_{\text{loss}} (\text{wt}\%) = 100 \times (W_0 - W_t) / W_0$, where W_0 is the initial weight and W_t is the weight of sample subjected to hydrolytic degradation for time t and drying in vacuum.

At least four measurements were performed for each sample and the average was reported.

3. Results and discussions

3.1. Synthesis and characterization of unzipped MWCNTs

The introduced functional groups in oxidatively unzipped CNTs were detected by FT-IR. As shown in Fig. 1, a band located at 1192 cm^{-1} (assigned to $-\text{C}-\text{O}-\text{C}-$ stretching [33]) appeared in $\mu\text{CNT-1}$ and became more significant in $\mu\text{CNT-2}$, $\mu\text{CNT-3}$, $\mu\text{CNT-4}$, and $\mu\text{CNT-5}$. Additionally, the bands around 1563 and 1718 cm^{-1} indicating carbonyl/carboxyl groups were introduced in these samples [34,35], and the gradual increment of the band intensities suggests that the modification was enhanced with increasing KMnO_4 amount.

Raman spectroscopy was also applied to characterize the μCNTs (Fig. 2). The CNTs display a D band at 1327 cm^{-1} , which originates from the disordered graphite structure or sp^3 -hybridized carbons of the nanotubes, and a G band at 1571 cm^{-1} , which is attributed to a splitting of the E_{2g} stretching mode of graphite. Meanwhile, a weak shoulder (D') of G band at 1608 cm^{-1} is also related to the extent of disorder in the nanotubes. The D/G intensity ratio (R) is often utilized to monitor the functionalization of CNT. In this work, it is found that the R increases with increasing amount of oxidant (from 0.94 of pristine CNT to 1.44 of $\mu\text{CNT-5}$), indicating that the more oxidant, the more functional groups or defects were generated in μCNTs [18]. This result is consistent with the above FT-IR and TGA measurements (see Fig. S1). The intensity of the D' band also increased after oxidation. Moreover, the G band of $\mu\text{CNT-3}$, $\mu\text{CNT-4}$ and $\mu\text{CNT-5}$ shifted to a higher frequency at 1597 cm^{-1} , and it was not able to distinguish the D' bands in these samples. We assume that the increased intensity of D' was the reason for this change. As the intensity of D' increased, it gradually merged with the G band, as shown in Fig. 2, and this merging between the G and D' caused the appearance of the shifting of G band.

In the XRD patterns, the CNT shows a peak at 25.9° , attributed to the (002) plane of the interplanar graphite spacings, corresponding to a d spacing of 0.34 nm (Fig. 3). With increasing oxidant content, the peak intensity decreased significantly and the 2θ value also decreased slightly. The d spacing increased (derived from the decrease in the 2θ values) might be due to the more functional groups generated between the adjacent layers during the process of oxidation. The peak of CNTs in these samples gradually decreased from $\mu\text{CNT-1}$ to $\mu\text{CNT-5}$, suggesting that the unzipping degree increased with increasing KMnO_4 . Moreover, for $\mu\text{CNT-5}$, the

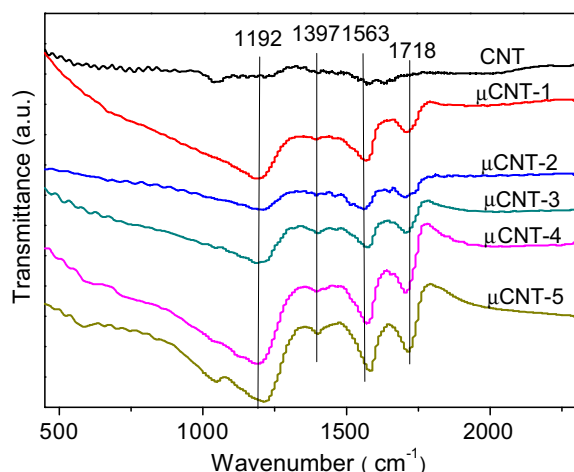


Fig. 1. FT-IR curves for pristine CNTs and oxidatively unzipped CNTs (μCNTs).

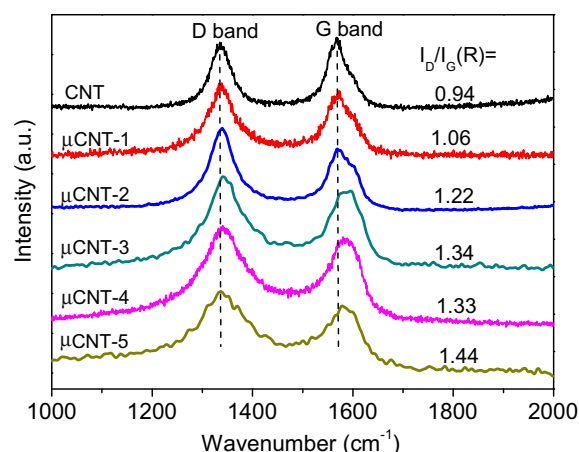


Fig. 2. Raman spectra and D/G intensity ratio (R , beside each curve) for pristine CNT and μCNTs .

disappearance of the characteristic peak of CNTs also implies the missing of integrity of the CNTs. This indicates that the unzipping process was almost complete in this sample [36].

TEM results provide the individual represented images in detail (Fig. 4). As compared to the untreated CNTs, the $\mu\text{CNT-1}$ was significantly shortened by oxidation from several micrometers to hundreds of nanometers, and the outer walls of $\mu\text{CNT-1}$ were partially loosened or unwrapped, but the whole CNTs' tube structure can still be clearly identified (Fig. 4C, D). With further oxidation, we can see that most of the CNTs walls possess unzipped structures. More interestingly, the length of $\mu\text{CNT-2}$ was not be further shortened as compared to $\mu\text{CNT-1}$. The TEM image of $\mu\text{CNT-3}$ (Fig. 4E, F) shows that the multiwalls of CNTs were opened to a higher degree with less inner tubes remaining. With a further increase in the KMnO_4 content, the length of $\mu\text{CNT-4}$ was not further decreased, comparable with $\mu\text{CNT-1}$ and $\mu\text{CNT-3}$ (not given). For $\mu\text{CNT-5}$, very thin layers were obtained (Fig. 4G, H) in TEM observation, and most of MWCNTs were cut and unzipped into small pieces. Thus, all of the above characterizations exhibited that unzipped MWCNTs with various features, including the surface functional groups, defects and shapes, with different unzipping degrees were successfully prepared.

3.2. Fabrication and characterization of PLLA/(μ)CNT nanocomposites

For these PLLA-matrixed nanocomposites including μCNTs with different oxidative degrees, the polymorphism is our first

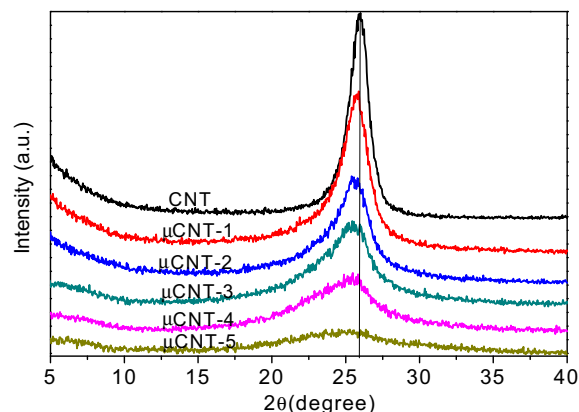


Fig. 3. XRD curves for pristine CNT and μCNTs .

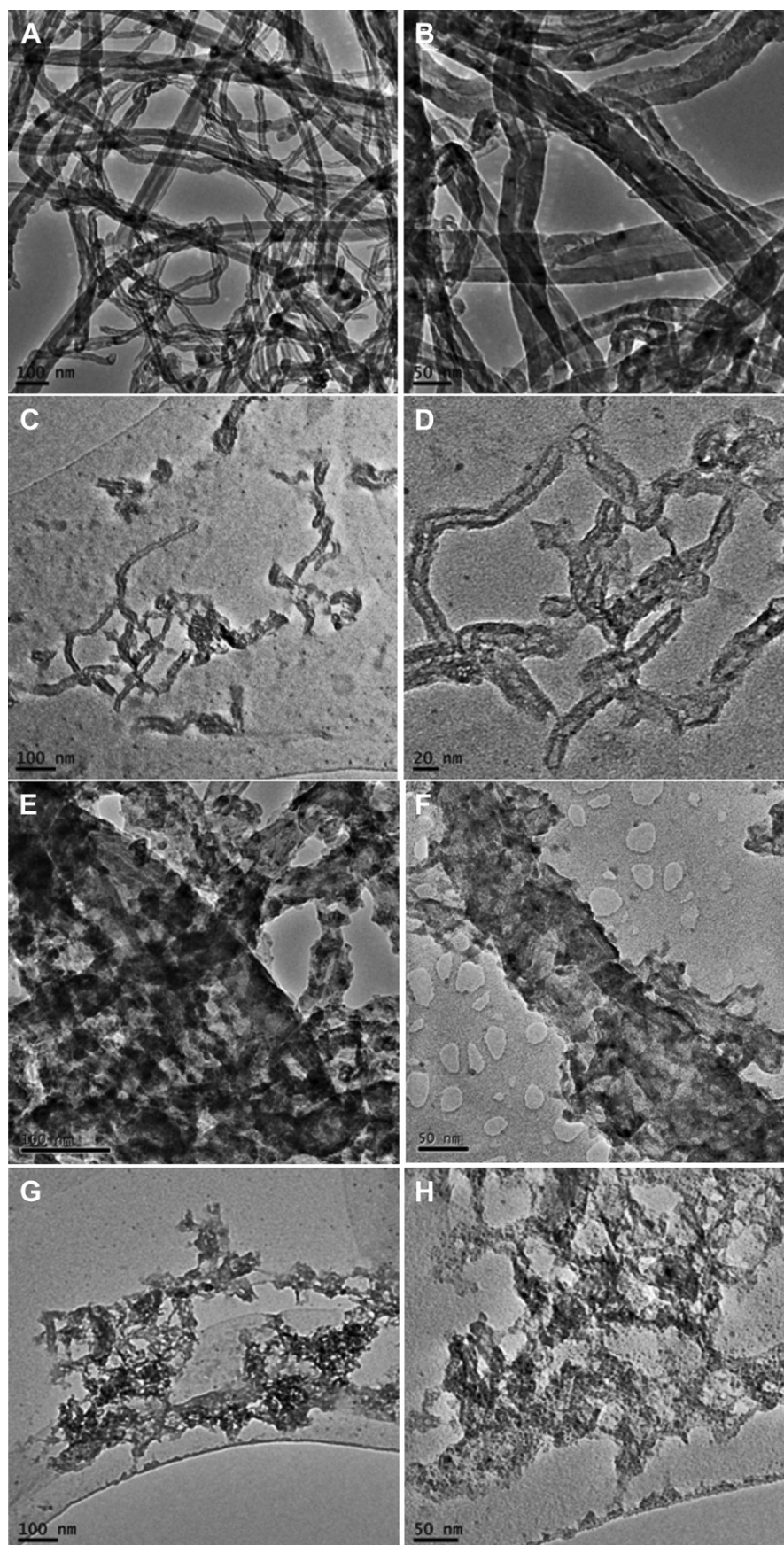


Fig. 4. TEM images of pristine CNT (A, B), μ CNT-1 (C, D), μ CNT-3 (E, F) and μ CNT-5 (G, H). B, D, F, and H are the enlargement of A, C, E, and G, respectively.

consideration. The PLLA, as reported, can crystallize in α , β and γ forms depending on the processing conditions. It forms the most common α form from the melt or solution under normal conditions, with a 10_3 helical chain conformation in which two chains interact to form an orthorhombic unit cell [37,38]. The FT-IR results, as shown in Fig. 5A, reveal a 921 cm^{-1} band assigned to the 10_3 helix (α crystal phase of PLLA) sensitive band, and a 955 cm^{-1} band ascribed to an amorphous band [39]. Therefore, this observation implies that all samples, including the neat PLLA were α -phase dominated, irrespective of the oxidative degree.

In addition, the broad peak that extends from 3000 cm^{-1} to 3500 cm^{-1} (ca. 3360 cm^{-1} in our case) was attributed to the $-\text{OH}$ functional groups from the carboxylic acid groups present in the μCNTs edges [40], which could form strong hydrogen bonding with PLLA, as widely reported for some polar polymers, such as poly(vinyl alcohol) [41], poly(methyl methacrylate) [42] and polyurethane [43]. In our case, this interaction between the μCNT and PLLA could be tentatively verified by the shift of the peak of $-\text{OH}$ stretching (Fig. 5B).

The XRD analysis can supply more conclusive information on the polymorphism of the samples, including the neat PLLA and PLLA/ μCNT nanocomposites. As shown in Fig. 5C, neat PLLA shows two weak characteristic diffraction peaks at around 16.25° and 18.57° , corresponding to (200)/(110), and (203) planes, respectively. For all PLLA/ μCNT composites, diffraction peaks (2θ) appear obviously at 15° , 16.7° , 19° and 22.8° , all being assigned to the α -phase modification. Meanwhile, no peak indicative of the β -phase e.g. 26° and 31° , appears. These observations signify the nucleation effect from the CNT and that all composite samples are α -phase dominated, which is consistent with the above IR results. Upon close checking, the diffraction peaks of the PLLA/ μCNT nanocomposites shift slightly to the lower angle as compared with those of neat PLLA, indicating that the corresponding interplanar spacings increase with the addition of MWNTs [44]. While the intensities of the diffraction peaks show no apparent change, indicative of the PLLA-matrix dependent state.

Dynamic mechanical analysis is another sensitive technique which enables one to acquire the information on the weak transition and/or interface of multiphase system [45]. In this case, the dynamic mechanical properties of neat PLLA and the nanocomposites were investigated and the temperature dependence of storage modulus (E') and loss factor ($\tan \delta$), the ratio of loss modulus to storage modulus, of neat PLLA and the PLLA/ μCNT nanocomposites are given in Fig. 6. As indicated, both neat PLLA and the nanocomposites exhibit a sharp reduction of storage modulus (E') around 55°C , corresponding to the glass transition of PLLA, and clearly, the variation of E' depends on the oxidation degree (Fig. 6A). The most interesting is, the maximum E' value of the PLLA/ μCNT -3 was ca. 1390 MPa , higher than the neat PLLA and all other alternatives (see the inset of Fig. 6A). As addressed above, the oxidation process would produce functional groups on the surface of CNTs, and in principle, this tendency should be enhanced with more oxidant. At the same time, however, the oxidation-induced breakage should be intensified, which could lead to more defects and agglomerations. This scenario will be more serious after considering the high viscosity of the polymer solution. Therefore, a proper oxidation degree is required in view of the two-edge effect from the oxidation unzipping process. This observation is more understandable considering the variation of crystallinity of PLLA, which will be further discussed in the following differential scanning calorimetry (DSC) characterization.

In addition, remarkable influence of CNTs on the $\tan \delta$ - T curves was well-resolved for the hybrids compared with that of neat PLLA (Fig. 6B). The lowered and slightly widened $\tan \delta$ peaks implied a more inner-structurally homogeneous material. In other words, the μCNTs were actually in a relatively uniform distribution in the PLLA matrix. This observation also implies that the modified μCNT interacts with the polymer matrix on a smaller scale, i.e., nano-scale level [46].

It is worth noting that: 1) From the E' - T curves, both neat PLLA and its nanocomposites show almost the same elastic modulus above 80°C , suggesting that the presence of μCNT does not

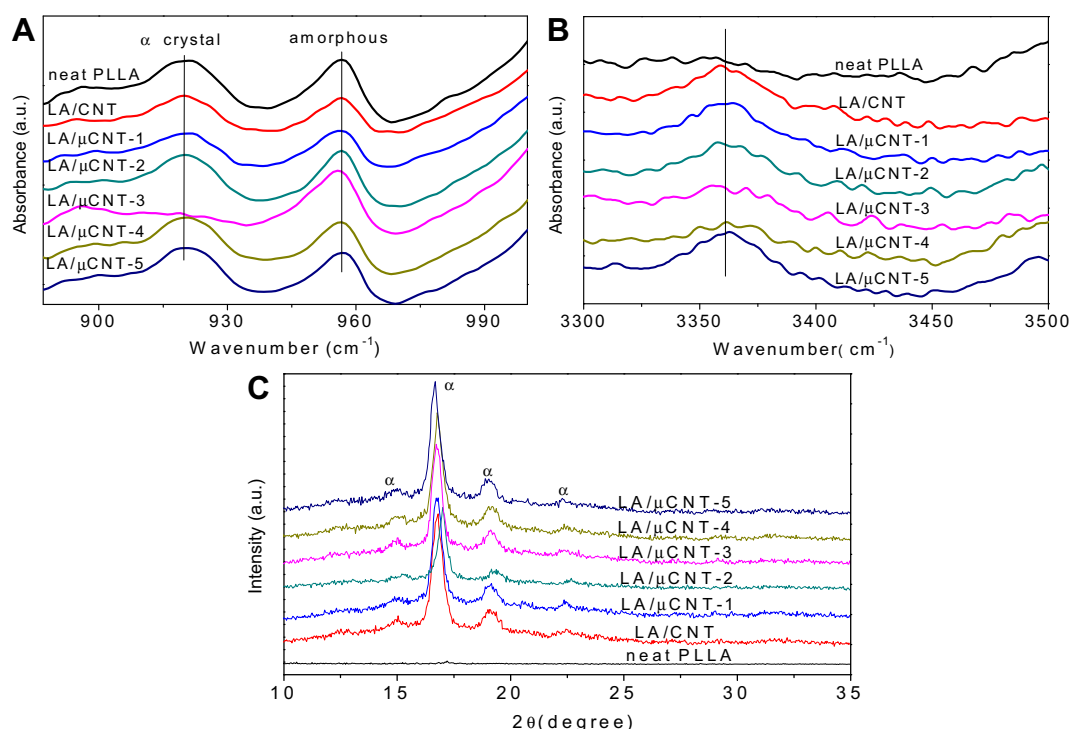


Fig. 5. FT-IR (A, B) and XRD (C) patterns for neat PLLA and PLLA nanocomposites with pristine CNT and μCNTs .

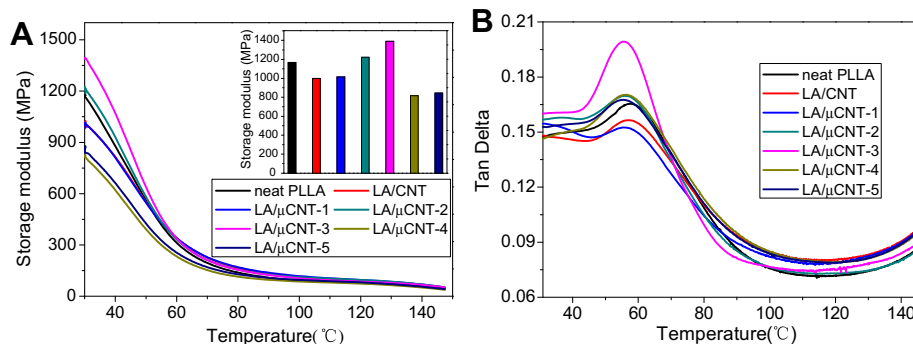


Fig. 6. The temperature curves of storage modulus (A) and $\tan \delta$ (B) for neat PLLA and PLLA nanocomposites comprising neat CNT and μ CNTs with different oxidative degrees. The maximum storage moduli of samples are given in the inset of A.

influence the elastic property of PLLA above the glass transition temperature. In the temperature range of 80–145 °C the storage modulus difference between neat PLLA and the PLLA/ μ CNT nanocomposite is very small, suggesting that the nanocomposite stiffness becomes matrix dependent. Similar observation was also found in recent publications, in which the effect of nanofillers, including clay [27], polyhedral oligomeric silsesquioxanes (POSS) [32], calcium carbonate [45], on the storage modulus becomes negligible above a specific temperature. 2) The concentration of oxidant (KMnO_4) does not lead to a significant shift and broadening of the $\tan \delta$ curves for the PLLA/ μ CNT nanocomposites compared with that of neat PLLA. We cannot give a sound interpretation to this aspect, but tentatively ascribe this to the low loading of μ CNT.

In general, load transferring strongly depends on the interfacial interaction between the fillers and the wrapped polymer matrix [45]. Additionally, as addressed above, the increased crystallinity of the PLLA matrix contributes a lot to the improved strength. Furthermore, the molecular-level dispersion of CNT in the PLLA matrix will favor the stress transferring across the CNT–PLLA interface. As a result, significant enhancement of storage modulus of the hybrids was achieved. This can be found from the case of PLLA/ μ CNT-2 and PLLA/ μ CNT-3 (Fig. 6A). However, under the over-oxidative condition, the interfacial interaction would be heavily weakened since the loosened and truncated CNTs may disable the load transferring.

Graphene has shown excellent thermal conductivity, with a measured k value of 3000 W mK^{-1} for a single-layer sheet at room temperature [47]. Therefore, its embedment in a polymer matrix is expected to significantly enhance the thermal conduction of the composites. Unfortunately, our TGA results (Fig. S1, in ESI) of PLLA and PLLA/ μ CNT composites do not show marked dependence of

thermal stabilities on the oxidation degree. This observation is ascribed to relatively low μ CNT loading, and the enhanced oxidation-induced defects, which will tremendously deteriorate the thermal conductivity and this in turn would lead to the nearly constant thermal decomposition temperature in the TGA tests.

The glass transition temperature (T_g) of polymer is affected by the mobility of polymer chains. DSC was used to investigate the T_g of the PLLA/ μ CNT nanocomposites (Fig. 7). The T_g of PLLA in the second scan is about 52.4 °C. With the addition of μ CNT, it increases gradually to 58.2 °C (Fig. 7A). The increase in T_g can be ascribed to an effective attachment of PLLA to the μ CNT sheets that constrains the segmental motion of the PLLA chains by hydrogen bonding and electrostatic attraction, as demonstrated in other reports [48,49].

The degree of crystallinities (χ_c) of neat PLLA and its nanocomposites are determined by the ratio of ΔH_m of the samples to that of 100% crystalline PLLA (ΔH_0), 93 J g^{-1} [50]. For clarity, the temperatures of major peaks, enthalpy of melting (ΔH_m) and the calculated χ_c from DSC thermograms of PLLA and hybrids are summarized in Table 1. Similar to the variation of E' values, the χ_c also displays a peak value for LA/ μ CNT-3 (ca. 47.1%). This observation also implies that an optimal oxidation degree is needed with respect to the crystallinity enhancement.

The increase of T_g and the enhanced χ_c , as also mentioned above in the XRD, FT-IR analysis, seem contradictory to the generally accepted fact that CNTs are effective nucleating agents that facilitate the crystallization of various polymers [51,52]. However, in our case, the copious, chemically functional group induced by the oxidation process, as well-resolved in the comparative FT-IR results in Fig. 1, will accordingly favor the generation of interaction sites between the μ CNT surface and PLLA segment. Meanwhile, the enhanced available interface areas (AIAs) with the μ CNT deduced

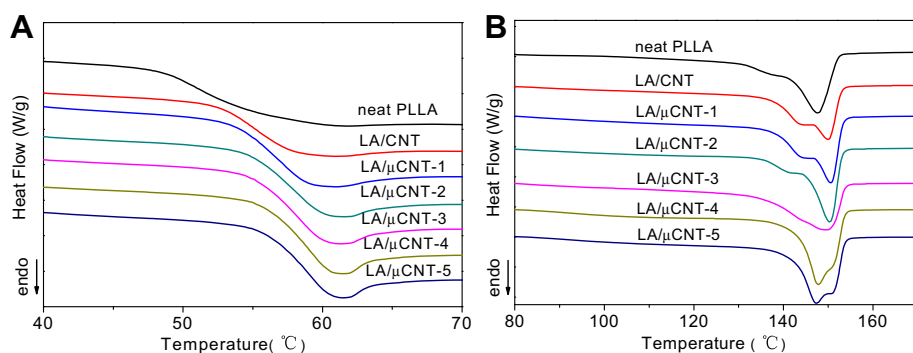


Fig. 7. DSC curves for neat PLLA and PLLA/(μ)CNT nanocomposites. The temperature range of 40–70 °C shows the T_g variation (A) and the temperature range of 60–170 °C shows the melting behavior (B). In this case, only the second DSC heating curves are collected.

Table 1

T_m , T_g , crystallinity and melting enthalpy of neat PLLA and PLLA/ μ CNT nanocomposites.

Sample	T_g , °C	χ_c , %	T_m , °C	ΔH_f , J g ⁻¹
PLLA	51.2	40.7 ± 0.6	139.1	37.9 ± 0.4
PLLA/ μ CNT	55.0	45.8 ± 0.4	140.6	42.8 ± 0.5
PLLA/ μ CNT-1	57.1	46.4 ± 0.3	143.1	43.3 ± 0.2
PLLA/ μ CNT-2	58.1	46.8 ± 0.1	143.6	43.8 ± 0.3
PLLA/ μ CNT-3	58.4	47.1 ± 0.2	143.7	44.0 ± 0.8
PLLA/ μ CNT-4	59.0	44.0 ± 0.4	142.8	41.1 ± 0.6
PLLA/ μ CNT-5	59.3	41.9 ± 0.5	141.6	39.2 ± 0.3

by the oxidation step, will certainly be beneficial to the molecular folding involved in the following crystallization step.

In general, good dispersion and interfacial stress transferring are important factors for preparing reinforcing nanocomposites, leading to a more uniform stress distribution and minimizes the presence of the stress concentration center [53]. However, over-oxidized CNTs may have negative effect. As discussed above, the oxygen-containing groups and negative charges on the CNTs surface can interact effectively with the PLLA through hydrogen bonding and electrostatic attraction. Moreover, the large aspect ratio of the μ CNT is also favorable to stress transferring. The improved compatibility, as reflected to some extent from the appearance of the as-prepared nanocomposites (Fig. S2, in ESI), and strong interaction between μ CNT and the PLLA matrix greatly enhance the dispersion of μ CNT on the molecular scale in PLLA matrix, as well as the interfacial adhesion, thus significantly increasing the mechanical properties of the nanocomposites.

3.3. The characterization of hydrolytic degradation

It is of great interest to study the effect of the addition of μ CNT on the hydrolytic degradation of PLLA. The variation of weight loss of neat PLLA and the PLLA/ μ CNT nanocomposite as a function of exposure time is presented in Fig. 8. The values of weight loss increase with prolonged exposure time for both neat PLLA and its nanocomposites. Moreover, the value of weight loss is always larger in the PLLA/ μ CNT nanocomposite than in neat PLLA, and this tendency is more evident with increasing oxidative degree for the CNT, i.e., in the order of PLLA/ μ CNT-5 > PLLA/ μ CNT-4 > PLLA/ μ CNT-3 > PLLA/ μ CNT-2 > PLLA/ μ CNT-1 $\approx$ neat PLLA. The ultimate values of the weight loss reach around 41.8 wt% for neat PLLA and 82.2 wt% for the PLLA/ μ CNT-5 nanocomposite, respectively, after 24 days exposure to NaOH.

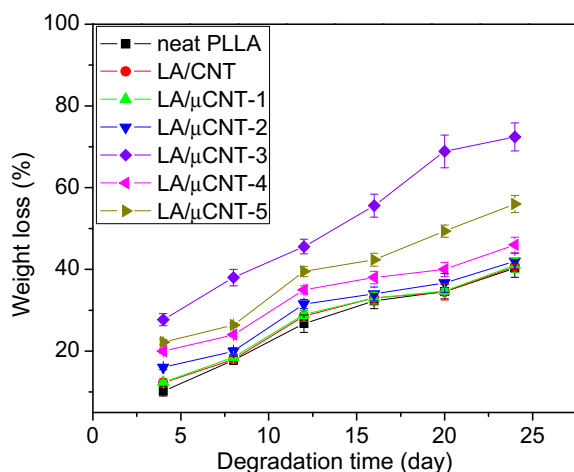


Fig. 8. Hydrolytic degradation of neat PLLA and PLLA/ μ CNT nanocomposites.

Given only the surface of the sample was eroded while the internal remained almost unchanged in the degradation process, the neat PLLA and its composites should undergo the surface erosion mechanism [54], and this speculation is corroborated further by our complementary GPC measurements, according to which no marked chain scission occurred. The M_w value ca. 2.53×10^5 g mol⁻¹ of neat PLLA prior to hydrolytic degradation decreased slightly to ca. 2.48×10^5 g mol⁻¹; for composites, the M_w values varied between 2.50×10^5 g mol⁻¹ and 2.64×10^5 g mol⁻¹ spanning of the hydrolytic-degradation time and oxidative degree of μ CNT. Therefore, the molecular weight during hydrolytic degradation was nearly unchanged.

The enhanced hydrolytic degradation of PLLA/ μ CNT may promote its wide practical applications as biomaterials and packing materials. It is well known that many factors may affect the degradation of aliphatic polyesters, such as pH, temperature, morphology, crystallinity, erosion mechanism, etc. In the present work, the same environmental conditions, i.e., pH and temperature were used in studying the hydrolytic degradation. So, the enhanced crystallinity, as reflected in the above FT-IR, XRD and DSC studies, of the nanocomposites could be the negative factor for the enhanced hydrolytic degradation. This observation also suggests, on the other hand, that crystallinity is not an influencing factor in the hydrolytic degradation of PLLA. Although similar results were also found by Okamoto et al. for the biodegradability study of PLLA and layered silicate nanocomposites [55], in which the crystallinity of neat PLLA is lower than those of nanocomposites, while the biodegradation rate of the latter is faster than that of the former. However, the exact origin of the enhanced hydrolytic degradation in the presence of μ CNT deserves further investigation.

4. Conclusions

In summary, a novel PLLA/oxidatively unzipped multiwalled carbon nanotubes (μ CNTs) nanocomposite was prepared via solution casting method in this work. Here, the oxidative unzipping process involves the lengthwise cutting and opening the walls of MWCNTs, which yielded separate ribbonlike graphene layers. The well dispersed μ CNT will effectively promote the crystallization of PLLA matrix, increase the interface areas, as well as the hydrolytic degradation of PLLA in the nanocomposites with respect to neat PLLA, which may be of great interest for the practical applications of PLLA.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.matchemphys.2012.03.113.

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