

## Review

# Crystalline Structure of Functionalized MWCNTs/Poly(L-lactide) Biodegradable Polymer Nanocomposites

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## Abstract

In this paper, well dispersed Multiwall carbon nanotubes (MWCNT)s were prepared by grafting of Poly (L-lactide) (PLLA) biodegradable polymer from the sidewall of aminated MWCNTs using oligomeric L-lactide (LA) (MWCNT-PLLA). After preparation of MWCNT-PLLAs/PLLA composites, the effect of MWCNT-PLLAs on crystallinity of PLLA was investigated by means of XRD, DSC and POM. It is found that the surface functionalization can effectively improve the dispersion and adhesion of MWCNTs as reinforcing filler in PLLA as polymer matrix and hence, improve the physical and thermo mechanical properties of nanocomposites. In addition, the results show that the addition of MWCNT-PLLAs increases the melting point and crystallinity of the composites. The MWCNT-PLLAs/PLLA composites show well-defined spherulites and the spherulite size increases with the increase of MWCNT-PLLAs concentration. The MWCNT-PLLAs decrease the mobility of matrix chains in amorphous phase of composites. It can be seen that the MWCNT-PLLAs increase the lamellae sizes and hence increase the crystallinity of PLLA polymer matrix. The grafted PLLA chains on the sidewall of MWCNTs, due to their orientation, increase the lamellae and spherulites in composites. It is predictable that the mechanical performance of composites increases due to two effects: the strength of MWCNTs in composites and the crystallization of PLLA matrix in composites.

**Keywords:** Biodegradable Polymer; Poly (L-Lactide); Functionalized Multiwalled Carbon Nanotubes; Crystallinity; Nanocomposites

## Introduction

Biodegradable polymers have been widely studied for various pharmaceutical and medical applications such as surgical sutures, tissue engineering and controlled drug delivery systems [1-3]. Poly (L-Lactide) (PLLA), poly ( $\epsilon$ -caprolactone) and their copolymer are linear aliphatic thermoplastic polyester, which they have intermediate mechanical properties, thermal plasticity, biodegradability and biocompatibility. However, one of drawbacks of such materials is that the mechanical properties of the polymer alone may be insufficient for high load bearing applications [4-6]. Reinforcing of biodegradable polymers can also be an approach

to overcoming some limitations of single applications of these materials, such as brittleness, low stiffness, and low toughness. Recently, there are some reports in preparation of MWCNTs/PLLA composite to increase the mechanical properties of these polymers [7-12].

Functionalization and manipulating of MWCNTs for biomedical applications are important for biomedical researchers [13,14]. The exceptional mechanical properties of CNTs have led to their use as effective reinforcing filler for polymer composites. The MWCNT based polymer composites have the potential for tailoring of unique lightweight materials with enhanced mechanical, physical, thermal, and electronic properties [15,16]. It is a prerequisite for effective reinforcement of polymer with CNTs to improve compatibility between them. For this reason, a number of studies on polymer/CNT composites have focused on improving the compatibility between CNTs and polymer matrix [17,18]. Functionalization or modification of MWCNTs has attracted increasing attention over the past years. Up to now, synthetic polymers and biomacromolecules have been grafted or assembled onto the sidewall of CNTs [19-22].

Tsuji et al. [23] investigated the effects of nano structured carbon fillers such as fullerene C<sub>60</sub>, single wall CNTs, carbon

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nanohorn, carbon nanoballoon, and conventional carbon fillers on conductivity (resistance), thermal properties, crystallization, and degradation of poly (L-lactide). Zhang et al. [24] reported the preparation of MWCNT/PLLA composite with the interaction between poly lactic acid (PLA) and MWCNTs occurring mainly through the hydrophobic C-CH<sub>3</sub> functional groups. Teoh [25] et al. fabricated electro spin nanocomposite scaffolds by encapsulation MWCNTs in poly lactic acid nanofibers in which the MWCNTs are aligned along the axis of the fibers.

Our research group [26-31] have functionalized pristine MWCNTs with some various procedures and then grafted PLLA form the side wall of the functionalized MWCNTs by ring opening polymerization using L-lactide as oligomer and St(Oct)<sub>2</sub> as initiator. In addition, the pMWCNTs were functionalized, at first, by Friedel Crafts acylation, which introduced the aromatic amine groups on the side wall of MWCNTs. Then, the PLLA chains covalently grafted from the sidewall of aminated MWCNTs. In this article, the effects of functionalized MWCNTs on physical and morphological properties of PLLA are reported to understand their structure property relationship.

## Experimental

### Materials

The L-lactide oligomer (Xiaogan Esun New Material Co, China) was used as received. Stannous octanoate (St(Oct)<sub>2</sub>) (Shanghai chemical reagent company, China) was used as a catalyst. Chloroform, ethanol, methanol, toluene, p-amino benzoic acid, poly phosphoric acid and phosphoric penta oxide (P<sub>2</sub>O<sub>5</sub>) were purchased from Kermel of China as analytic reagent. The pristine MWCNTs (pMWCNTs) were purchased from the Nanotech Port Company. The diameter of MWCNTs is 5-20 nm, length is 5-15 μm and special surface area is 40-300 m<sup>2</sup> g<sup>-1</sup>.

### MWCNTs Functionalization

The p-amino benzoic acid, pMWCNTs and poly phosphoric acid were heated at 120°C for 3 h. Then, P<sub>2</sub>O<sub>5</sub> was added to the mixture, and then the mixture was heated for 12 h. The reacted mixture was cooled and diluted with distilled water, and the precipitates were washed with the ammonium chloride solution. Then, the aminated MWCNTs (MWCNT-NH<sub>2</sub>)s were washed with distilled water and then vacuum-filtered through a 0.22 μm millipore polycarbonate membrane. The filtered solid was dried in oven at 50°C over night. For grafting of PLLA form the sidewall of aminated MWCNTs (MWCNT-PLLAs), the L-lactide oligomer were added into a flask with Sn(Oct)<sub>2</sub> as initiator and MWCNT-NH<sub>2</sub> as co initiator. The flask was sealed under vacuum and then placed in an oven at 140 °C for 48 hours. The ungrafted PLLA chains and monomers were removed by dissolution of synthesized materials in chloroform and vacuum-filtered through a 0.22 μm Millipore polycarbonate membrane four times. Then the products were dried in an oven at 40°C for 2 days [31].

### Nanocomposites Preparation

The MWCNT-PLLAs, which were dispersed in chloroform with various concentrations, were mixed with the solution of neat PLLA

in chloroform to achieve MWCNT-PLLAs/PLLA composites having 0.5, 1.0, 2.0 and 3.0 and wt % loading of MWCNT-PLLAs. The neat PLLA homopolymers were prepared as introduced in our previous works [28-31]. The mixtures were left in glass molds three days at room temperature for chloroform evaporation, then the glass molds contains composite films were dried in an oven at 40°C for 2 days to completely evaporation of solvent. The film of composites were removed from glass molds and cut for characterization.

### Materials Characterization

The molecular weight and the distribution of the synthesized PLLA was measured by gel permeation chromatography (GPC) using Agilent 1100 series (Agilent, USA). Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1.0 mL/min at 30°C. The RI Mobile Phase detector with two columns Agilent 79911GP-101 and 79911GP-104 (connected in series) are carried out. Calibration was performed with polystyrene (PE) standards to determine the absolute weight-average ( $M_n$ ), number-average molecular weight ( $M_w$ ) and polydispersity index (P.I.) of prepared neat PLLA. For sample preparation, 40 mg of prepared PLLA is solved in 20 ml of THF and magnetic stirrer used for 5 hours to find homogenous solution. The molecular weight of prepared PLLA is characterized using GPC. It is found that the  $M_w = 272625$ ,  $M_n = 147641$  and P.I.=1.84. It means that the prepared polymer has a good quality.

The X-ray diffraction (XRD) was employed to investigate the crystalline structure of neat polymer and composites using a Rigaku D/max-rb rotating anode X-ray diffractometer at 50 kV and 40 mA. The morphology and spherulite pattern of the polymer and composite thin films were studied with an Zeiss polarized light optical microscope (POM) (Axiotech) equipped with Olympus digital camera to save the images in computer. Samples of neat PLLA and its composites with various concentrations of MWCNT-PLLAs were sandwiched between two cover glasses and heated on a hot stage at premelting temperature, 160°C. Each sample was pressed into a thin film with a thickness of approximately 0.03 mm, kept for 30 min to eliminate any thermal history and the memory of the crystalline form in the melt, and then cooled to room temperature at a cooling rate of 2 °C/min. Transmission optical microscope is used to assess the uniform dispersion of MWCNTs in PLLA composites. In a transmission optical microscope (OM), light is transmitted through the sample and this allows us to probe dispersion of CNTs inside the sample. In the OM, light is transmitted through the sample and allows us to probe dispersion of MWCNT-PLLAs in composites.

The Differential Scanning Calorimetry (DSC) was carried out with a Perkin-Elmer Diamond DSC. Samples (10 ± 0.5 mg) were placed in aluminum crucibles. An empty aluminum crucible was used as reference. Samples were heated from -30 °C to 200 °C at flow of N<sub>2</sub>. Heating rate 20°C min<sup>-1</sup> was used and continuous recordings of the heat flow and sample temperature were taken. The thermo gravimetric properties of prepared materials were investigated using a simultaneous thermal analyzer (ZRY-2P) by scanning from 30 to 600°C at heating rate of 20°C\*min<sup>-1</sup> under nitrogen atmosphere.

## Results and Discussions

### PLLA/MWCNTs Morphology

(Figure 1) presents the transmission optical micrographs of MWCNT-PLLAs/PLLA and pMWCNTs/PLLA composites with 1 wt% concentration of MWCNT-PLLAs and pMWCNTs, respectively, at low and high magnification. The black regions in optical images refer to the agglomerated MWCNTs. Figure 1(a) and 1(b) show that the size and the concentration of agglomerated MWCNT-PLLAs is small which indicate that the MWCNT-PLLAs can disperse homogeneously in the PLLA polymer matrix. The entanglements of MWCNT-PLLAs are just due to the length of filler and random orientation in composite solution. However, a poor degree of dispersion and highly agglomerated clusters of pristine MWCNTs in PLLA can be observed in (Figure 1(c) and 1(d)). The reasons that the agglomerated and entangled points of MWCNT-PLLAs are significantly smaller than pMWCNTs can be explain as fellows. The MWCNT-PLLAs has relatively good dispersibility in PLLA polymer by solution casting technique due to its homogenous dispersibility in chloroform. The optical images reveal that the functionalization of MWCNTs significantly decreased the agglomeration of MWCNTs in composites.

### PLLA/MWCNTs Crystallinity

The XRD patterns of pristine and functionalized MWCNTs are shown in Figure 3. The pattern of the pristine MWCNTs shows three peaks. As shown in Figure 2(1), the diffraction at  $21^\circ$  is attributed to the impurities such as amorphous carbon. The peaks at  $26.05^\circ$  and  $39.3^\circ$  are corresponding to the  $(3.47, 002 \text{ \AA})$  and  $(100, 2.12 \text{ \AA})$  reflections of the carbon atoms, respectively. They refer to the walls of MWCNTs in Figure 2(2) from the graphene plains. The XRD patterns of MWCNT-NH<sub>2</sub> display the presence of two peaks at  $26.05^\circ$  and  $42.7^\circ$  ( $2.12 \text{ \AA}$ ) corresponding to the (002) and (100) reflections from the graphene plains. It can be seen that the diffraction peaks of amorphous carbon decrease because of purification during amination. As can be seen in Figure 2(3), the XRD pattern of MWCNT-PLLAs shows two significant diffraction peaks at  $16.7^\circ$  and  $19.06^\circ$  which characterize the crystallinity of PLLA grafted polymer chains on the sidewall of MWCNTs (Figure 2(4)).

The XRD pattern of the neat PLLA and its composites with various concentrations of MWCNT-PLLAs are shown in Figure 3. The d-value of neat PLLA and its composites with various concentrations of MWCNT-PLLAs are summarized in (table 1)

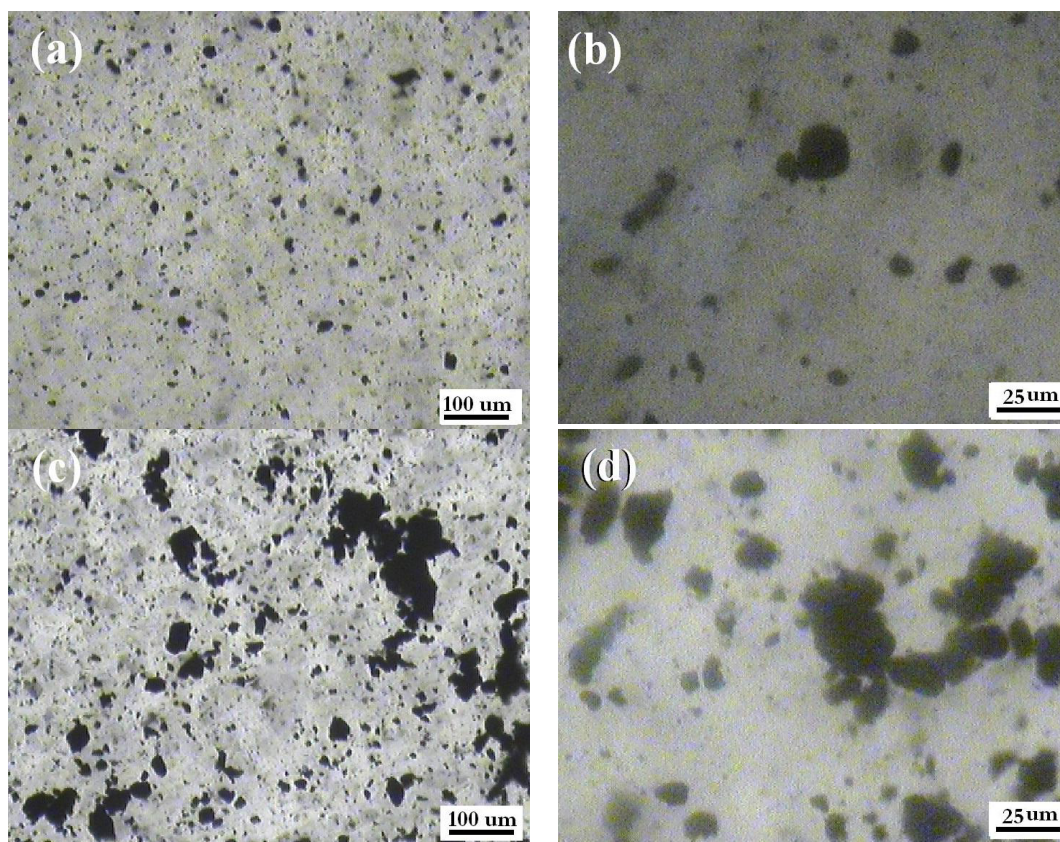
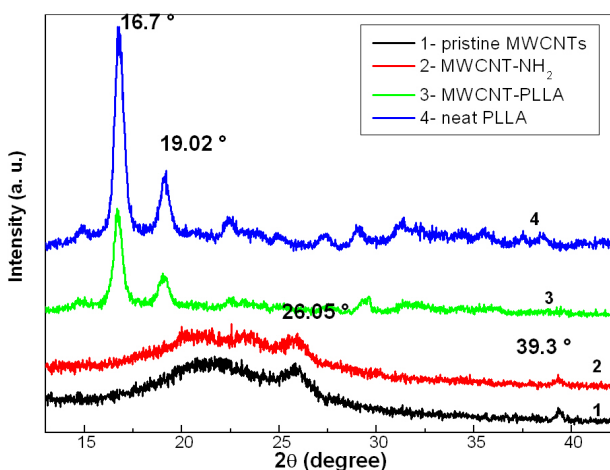


Figure 1: Optical micrographs of composite films: (1%)MWCNT-PLLAs/PLLA (a) and (b), (1%)pMWCNTs/PLLA (c) and (d)

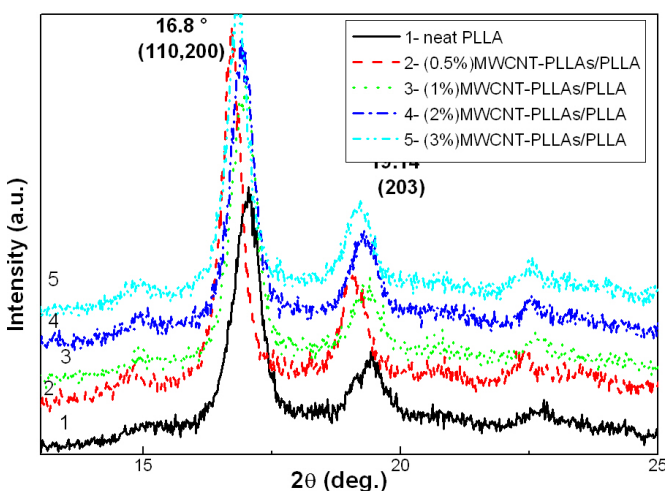
Filler contents (wt%)	d-value (nm)
0	5.20
0.5	5.20
1	5.22
2	5.235
3	5.26

**Table 1:** The d-value of neat PLLA and its composites with various concentrations of MWCNT-PLLAs

As can be seen, the diffraction patterns of neat PLLA show there are two significant diffraction peaks at 17.02° and 19.48° which characterize the crystalline phase of neat PLLA. Depending on processing conditions, PLLA can crystallize in  $\alpha$ ,  $\beta$  and  $\gamma$  forms. Crystallization of PLLA from the melt or solution results in its most common and stable polymorph, the  $\alpha$  form, characterized by two anti parallel chains in a left-handed  $10_3$  (or distorted  $10_3$ ) helix conformation packed in an orthorhombic (or pseudo-orthorhombic) unit cell. It is found that the increment of MWCNT-PLLAs do not change the crystalline form of PLLA [32].



**Figure 2:** The XRD patterns of pristine MWCNTs (1) MWCNT-NH<sub>2</sub>s (2), MWCNT-PLLAs (3) and neat PLLA (4)

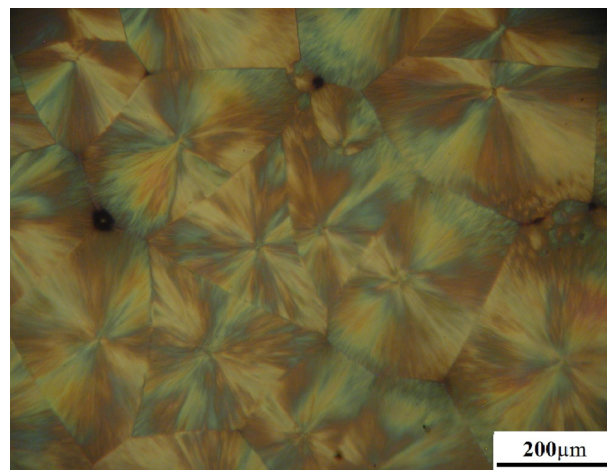


**Figure 3:** X-ray diffraction patterns of neat PLLA and its composites with various amounts of MWCNT-PLLAs

While, increase the intensity of diffraction peaks. In addition, the diffraction peaks of PLLA shifted to lower degree with increment the concentration of MWCNT-PLLAs in composites. It is found that the MWCNT-PLLAs increase the crystallinity of composites. The shift of diffraction peaks to lower degree is due to increasing the d-value and hence increasing the size of lamellae in composites. The d-value refer to the diffraction peak at 17.02° give a good information about the lamellae sizes. Table 1 shows the d-value of the diffraction peak at 17.02° of neat PLLA and its composites with various concentrations of MWCNT-PLLAs. The d-value that extracted from the diffraction pattern of PLLA and composites is proportional to the size of lamellae. It can be seen that the MWCNT-PLLAs increase the lamellae sizes and hence increase the crystallinity of PLLA polymer matrix. The lamellae size of MWCNT-PLLAs/PLLA composites slightly increases with the further increasing the concentration of MWCNT-PLLAs. The diminishing of FWHM is related to the increment of lamellae sizes of crystalline phase in composites.

### Spherulite Formation of MWCNT-PLLAs/PLLA Composites

(Figure 4) gives the polarized optical microscopy (POM) photomicrographs of spherulites of neat PLLA. It can be seen that the range of the spherulites size of net PLLA is from 200  $\mu$ m to 500  $\mu$ m and the spherulites are well-defined spherulites and they have uniform distribution. Figure 5 shows the POM photomicrographs of MWCNT-PLLAs/PLLA composites with various concentrations of MWCNT-PLLAs. It is found that the MWCNT-PLLAs/PLLA composite films are covered with well-defined spherulites. It means that the considered crystallization temperature and crystallization time for this purpose is adequate. The range of the size of spherulites in composites is increases with increasing the concentration of MWCNT-PLLAs in composites. The size increment of spherulites is due to earlier crystallization of some nucleation points. In the semi crystalline polymer such as PLLA, the nucleation points start to crystallize from melt region. The nucleation points are divided to two groups, homogenous and heterogeneous [33-35].



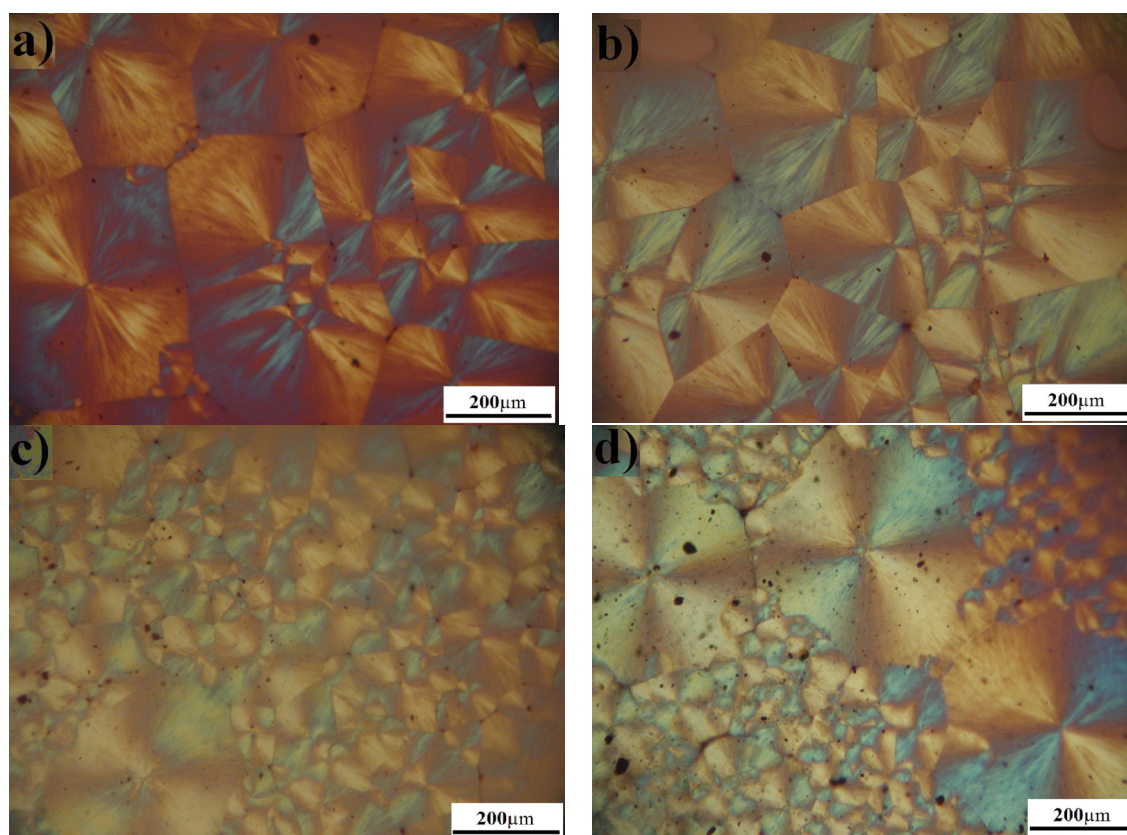
**Figure 4:** The POM photomicrograph of neat PLLA

The MWCNT-PLLAs are heterogeneous nucleation points in MWCNT-PLLAs/PLLA composites. The spherulite formation

of composite with 3 wt% of MWCNT-PLLAs is very near to that of (2%)MWCNT-PLLAs/PLLA composites. While the size and density of agglomerated points of fillers in (3%)MWCNT-PLLAs/PLLA are higher than that of (2%)MWCNT-PLLAs/PLLA. It can be seen that the range of the spherulites size of MWCNT-PLLAs/PLLA composite is from 50  $\mu\text{m}$  to 800  $\mu\text{m}$  and the spherulites have not uniform distribution. Some of spherulites are too large. It means that the large spherulites are grown earlier than small spherulites. The nucleation point of large spherulites are cluster of entangled MWCNTs. This effect shows that there is a limitation for adding the MWCNT-PLLAs to polymer for enhancing the considered physical and mechanical properties of composites. The black points refers to the agglomerated MWCNT-PLLAs. The size and density of agglomerated points are increase with increasing the concentrations of MWCNT-PLLAs in composites.

(Figure 6) shows the spherulites that created with the two forms of agglomerated MWCNT-PLLAs in composites. The results show that the presence of MWCNT-PLLAs accelerates the overall crystallization of PLLA during heating and cooling. The increment

in the size of spherulites with further increment of MWCNT-PLLAs is due to higher crystallization temperature of heterogeneous nucleation points. In addition, it is found that the larger nucleation points start to crystallize earlier than the smaller nucleation points. The orientation of grafted PLLA chains on the sidewall of MWCNT-PLLAs accelerate the crystallization of matrix PLLA chains in composites. Crystalline polymers build up complex structural entities, which blend amorphous and crystalline domains at a very small scale ( $\approx 10 \text{ nm}$ ). The coexistence of domains, which are of molecular, dimensions stems from the fact that the chains tend to fold upon crystallization: this chain folding is a characteristic feature of polymers, and creates an organizational scale which is unique to polymers. It induces a small scale subdivision of the polymer space, and makes it necessary to describe the structure of crystalline polymers at three different length scales: at the level of the unit-cell. Structural investigations of semi-crystalline polymers has focused on the structure of the lamellae, the impact of chain folding, the organization of these bi-dimensional lamellae in more complex three-dimensional entities (the spherulites), in the possibility to reduce or eliminate the amorphous zones to



**Figure 5:** The POM photomicrograph of MWCNT-PLLAs/PLLA composites with various concentrations of MWCNT-PLLAs: 0.5 wt% (a), 1 wt% (b), 2 wt% (c) and 3 wt% (d)

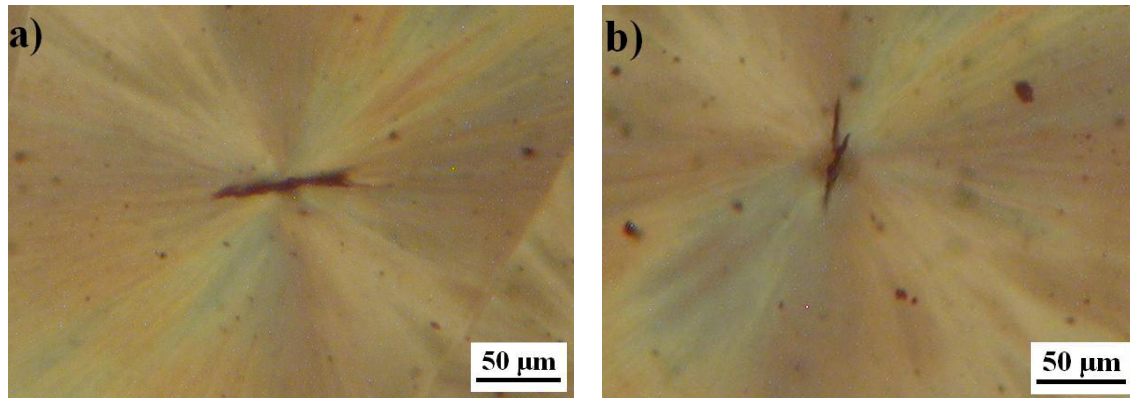


Figure 6: The MWCNT-PLLAs as heterogeneous nucleation agents at the center of spherulites

reach and exploit the much superior mechanical properties of the crystalline core. Increment in mechanical performance, specially yield strength and ultimate strength of composites is related to the crystalline phase of polymer more than that of amorphous phase. Of course, the MWCNT-PLLAs enhance the mechanical strength of both of crystalline phase and amorphous phase of composite.

(Figure 7) shows the DSC curves of neat PLLA and its composites with various concentrations of MWCNT-PLLAs as reinforcing fillers. The melting point and melting enthalpy of MWCNT-PLLAs/ PLLA composites that extracted from the DSC curves are presented in (table 2) It can be seen that the melting point of composites increases with increasing the concentration of MWCNT-PLLAs in composites. The increment in melting point is due to increasing the crystalline phase of composites. The increasing in concentration of MWCNT-PLLAs increases the size and density of lamellae in composites. Hence, the increment in melting point of composites is due to increment the concentrations of lamellae and increment in the thickness of lamellae [36].

Filler contents (wt%)	Melting point (°C)	Melting Enthalpy (J/g)
0	175.7	26.37
0.5	176	26.95
1	178	27.65
2	178.7	29.11
3	180.4	29.92

Table 2: The melting point and melting enthalpy of neat PLLA and its composites with various concentrations of MWCNT-PLLAs

Additionally, the MWCNT-PLLAs increase the viscosity of PLLA polymer matrix. It reveals that the crystallinity of composites increases with increasing the concentrations of MWCNT-PLLAs/ PLLA composites. Increasing the crystallinity and viscosity of PLLA increases the melting point of PLLA. As can be found from table 2, the reinforcing filler increase the melting enthalpy of composites, which refers to increasing the size and density of lamellae of PLLA chains in composites.

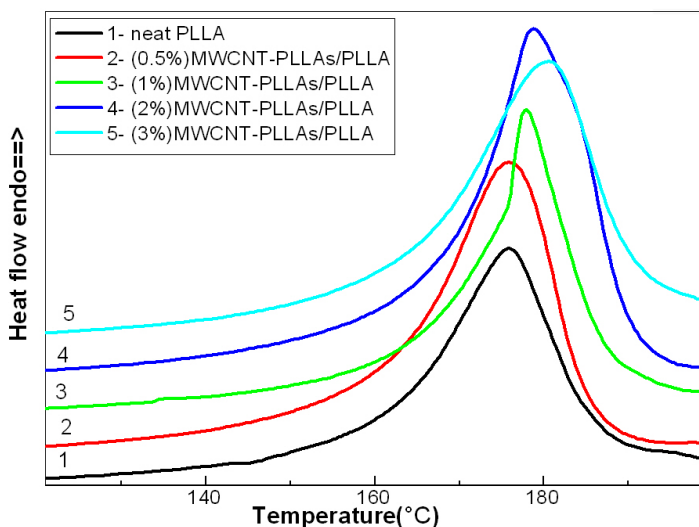


Figure 7: The DSC curves of neat PLLA and it's composites with various concentrations of MWCNT-PLLAs

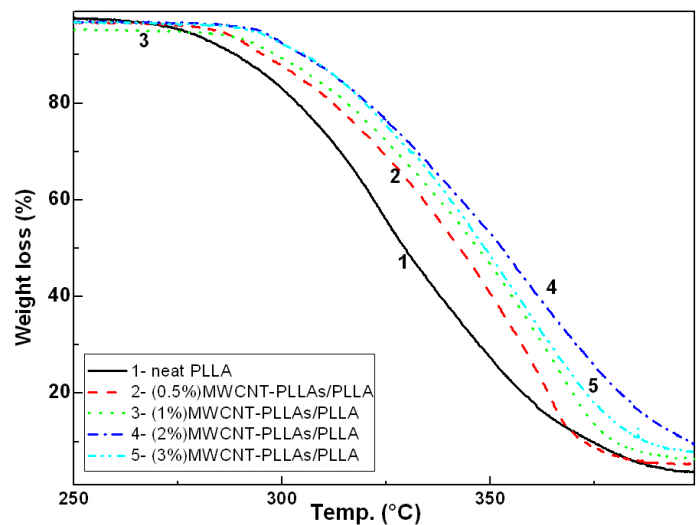


Figure 8: The TGA of neat PLLA and its composite with various concentrations of MWCNT-PLLAs.

The TGA analysis results of neat PLLA and its composites with various concentrations of MWCNT-PLLAs are presented in Figure 8. The TGA plots shows a single peak corresponding to the maximum rate of weight loss for degradation temperature. The decomposition of PLLA molecular chains start from 275 °C and finish at 400 °C. The results indicate that incorporation of MWCNT-PLLAs increases the thermal stability of the PLLA. The composites show a higher thermal degradation peak temperature and larger amount of residue at the end of the degradation compared with neat PLLA. It reveals that the thermal stability of MWCNT-PLLAs/ PLLA composites increase with increasing the concentrations of MWCNT-PLLA up to 2 wt%.

## Conclusions

The grafted PLLA polymer chains effectively improve the dispersion of MWCNTs in PLLA polymer matrix. The incorporation of MWCNT-PLLAs (up to 2 wt%) with PLLA increases the crystallinity of composites. Further increment in concentrations of MWCNT-PLLAs, increases the agglomeration of MWCNTs in composites. Increment in agglomeration of MWCNTs, diminishes the physical and hence mechanical performance of composites. The increment in crystallinity refers to increasing the density and sizes of lamellae in MWCNT-PLLAs/PLLA composites. The MWCNT-PLLAs as heterogeneous nucleation agents creates lamellae and spherulites during the crystallization of composites earlier than that of homogenous nucleation agents. The finding of significant effect of functionalized MWCNTs on properties of PLLA may widen the way to further research and applications for these multifunctional polymers especially for hard tissue engineering such as bone fixation. It can be predict that the mechanical performance of composites increases due to two effects, the strength of MWCNTs and the crystallization of PLLA matrix in composites. In addition, the combination of biodegradable polymers and MWCNTs opens in fact a new perspective in biomedical applications.

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