Synthesis and characterization of bionanocomposites of poly(lactic acid) and TiO2 nanowires by in situ polymerization

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Bionanocomposites from biopolymers and inorganic nanoparticles are of great interest for packaging materials due to their enhanced physical, thermal, mechanical, and processing characteristics. In this study, poly(lactic acid) (PLA) nanocomposites with covalent bonding between TiO2 nanowire surface and PLA chains were synthesized through in situ melt polycondensation. Molecular weight, structure, morphology, and thermal properties were characterized. Fourier transform infrared spectroscopy confirmed that PLA chains were covalently grafted onto TiO2 nanowire surface. Transmission electron microscopy images also revealed clearly a third phase presence on the nanowires after the grafting process. Those grafted PLA chains exhibited significantly increased glass transition temperature and thermal stability, compared with pure PLA. The weight-average molecular weight of PLA/2% TiO2 nanowire bulk nanocomposites increased by 66% compared with that of pure PLA. The electron microscopy results showed that strong interfacial interaction and homogeneous distribution were achieved between inorganic nanowires and organic PLA matrix in the bulk nanocomposites. The PLA matrix in bulk nanocomposites exhibited elevated glass transition temperature and decreased crystallization ability as the TiO2 nanowire concentrations were increased from 0 to 2%.

1. Introduction

Packaging has been one of the rapidly growing areas for the use of plastics. Out of total plastics production, 41% are used in packaging industry, and 47% are used for food packaging [1], which are mainly short-term and single use items. The currently used plastics are mainly made from petroleum based polymers, of which the major concerns are their issues of being non-biodegradable and having non-renewable sources. Poly(lactic acid) (PLA), derived from renewable sugar based resources (starch, sugar cane, cellulose, etc.), has shown great potential as a biodegradable packaging plastic [2,3]. However, the low glass transition/heat distortion temperatures around 60 °C and slow biodegradation rate have severely limited its broad disposable applications [4,5].

Inspired by Toyota researchers in the early 1990s who added 4.7% nano-clay into nylon 6 resulting in about 50% increase in the strength/modulus and 87 °C increase in the heat distortion temperature [6,7], synthesizing polymer nanocomposites (PNCs) offers a new approach to enhancing the physical, thermal, and mechanical properties of pristine polymers [8–11]. PLA nanocomposites have been reported using various nanoparticles, including carbon nanotubes, layered silicates or clays, silica, graphite, polyhedral oligomeric silsesquioxane, magnesium oxide, etc [12–18]. Though those nanocomposites exhibited enhanced mechanical strength, very few nanoparticles could efficiently improve the glass transition temperature (Tg) and degradation rate of PLA [18,19] because of the lack of strong interfacial interactions between nanoparticles and PLA matrix and the lack of effective degradation promoters.

Because of the capability of absorbing UV light (λ < 388 nm) to generate oxygen species [20,21], TiO2 nanoparticles have been applied to promote the photodegradation of various organic chemicals such as aldehyde, toluene, and benzene [22]. Once TiO2 nanoparticles are incorporated into polymer matrix, these active oxygen species will lead to photodegradation reaction by attacking the interfacial polymer chains, forming carbon-centered radicals, and accelerating chain cleavage. Zan and co-workers incorporated TiO2 nanoparticles into polyethylene and polystyrene, and they reported significant photodegradation of polymer matrix after UV irradiation for a period of time [21,23]. Although biodegradation of PLA can be advanced in the ground with appropriate moisture and bacteria, it

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still requires a long period of time [24,25], and this biodegradation does not advance in the air. By adding photosensitive TiO2 nanoparticles into biodegradable PLA, PLA nanocomposites can possess both photodegradability and biodegradability [14], and thus the degradation can be promoted under any conditions. Recent advances make it possible to synthesize considerable quantities of TiO2 nanowires [26–28]. The extended nanoparticles (i.e., nanowires) can more easily form network structures through either direct interaction or chain bridging between the nanoparticles, which is believed to play a significant role in property enhancement [11,29], compared with conventional nanospheres. Furthermore, large quantities of hydroxyl groups on the TiO2 nanoparticle surface enable it to be functionalized with organic monomers or grafted with polymer chains [30–35].

The two challenges of synthesizing PNCs with targeted properties are the difficulties in achieving nanoscale homogeneous dispersion and strong interfacial interaction between nanoparticles and polymer matrix because nanoparticles typically agglomerate due to their hydrophilic nature and high surface area, and they are not miscible with hydrophobic polymer phase [8,36]. In order to solve these problems, we first dispersed TiO2 nanowires into hydrophilic lactic acid with the aid of ultrasonic treatment and mechanical stirring. Carboxylic acid was known to bond to TiO2 with each of its oxygen atoms to a TiIV center of the surface in a bridging bidentate mode [31,32,37]. Once the carboxyl group of lactic acid is covalently bonded to the surface of TiO2 nanowires, the remaining hydroxyl group can form ester bonds with another lactic acid. The polymer chains continue growing on the nanowire surface with removal of resultant water during condensation polymerization (as illustrated in Fig. 1). Using the similar approach, we previously grafted PLA chains onto hydroxylated MgO nanocrystals and synthesized PLA/MgO bulk nanocomposites with satisfied interfacial interaction and nanoscale dispersion of nanocrystals into PLA matrix [38]. The specific objectives of this study are to (1) synthesize photocatalytic TiO2 nanowires and characterize the properties; (2) synthesize PLA/TiO2 nanowire nanocomposites via in situ melt polycondensation from lactic acid with different TiO2 nanowire loadings; (3) characterize the properties of PLA-grafted TiO2 (PLA-g-TiO2) nanowires isolated from free PLA in the PLA/TiO2 nanowire bulk nanocomposites to confirm the surface polymerization; and (4) characterize the molecular weight, structure, morphology, and thermal properties of the bulk nanocomposites.

2. Experimental

2.1. Materials

L-lactic acid was supplied as a 90 wt% aqueous solution by Acros Organics. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) was purchased from Fisher Scientific. Absolute ethanol was obtained from Decon Laboratories. Titanium dioxide (TiO2) nanopowders (<100 nm, mixture of rutile and anatase TiO2), Tin (II) chloride dihydrate (SnCl2·2H2O) (98%, reagent grade), and p-toluenesulfonic acid monohydrate (TSA) (98.5%, ACS reagent grade) were purchased from Sigma–Aldrich Co. All materials were used as received.

2.2. TiO2 nanowires synthesis and characterization

Several ways have been indicated in the literatures to synthesize TiO2 nanowires [26–28]. We followed a simple chemical approach described by Zhang et al. [39]. For a typical preparation, 0.1 g TiO2 nanopowders were placed into a Teflon-lined autoclave of 50 ml capacity. It was then filled with 40 ml 10 M NaOH aqueous solution, sealed into a stainless steel tank and maintained at 200 °C for 24 h without stirring. After cooling down, the sample was washed with 1 M aqueous HCl solution, deionized water, and absolute ethanol several times and dried at 80 °C for 12 h. Finally, we obtained soft fibrous TiO2 nanowires with white color. The Brunauer-Emmett-Teller (BET) surface area and porosity structure were determined with a Micromeritics instrument (TriStar-3000). The nitrogen adsorption isotherms were obtained at 77 K. The X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 instrument, using Cu–Kα radiation set at a voltage of 40 kV and a current of 40 mA. The scans ranged from 10 to 90°, with a scanning rate of 6°/min. The optical absorption of the synthesized TiO2 nanowires was measured on a UV–vis spectrophotometer (U-3010, Hitachi, Japan).

2.3. Dehydration/oligomerization

Our preliminary results showed that the addition of TiO2 nanowires should be less than 2 wt% to achieve homogeneous dispersion in the LA monomer. A determined amount of TiO2 nanowires (0.25, 0.5, 1, and 2 wt%, based on the weight of pure lactic acid) were added gradually to 30 g of a 90 wt% aqueous solution of LA and ultrasonically treated for 30 min. The mixture was then transferred into a 100-ml three-neck flask equipped with a mechanical stirrer and a reflux condenser that was connected with a vacuum system through a liquid nitrogen cold trap. The mixture was first dehydrited at 110 °C under atmospheric pressure for 2 h, then at 130 °C under a reduced pressure of 100 torr for 3 h, and finally at 150 °C under a reduced pressure of 10 torr for another 4 h. Then a viscous oligomer with TiO2 nanowires was obtained. Oligomer without TiO2 nanowires was also prepared as a control following the same procedures. The oligomer yield (weight of oligomer divided by the weight of pure lactic acid and TiO2 nanowires) resulting from this step was about 72% on average.
2.4. Polymerization

After cooling down, the oligomer from the previous step was mixed with SnCl2·H2O (0.4% wt relative to oligomer) and TSA (an equimolar ratio to SnCl2·H2O) as a binary catalyst [40]. The mixture was gradually heated to 180 °C with stirring speed of 200 rpm. The pressure was reduced gradually to 10 torr in 1.5 h. Then the reaction was continued at 180 °C/10 torr for 10 h with stirring speed of 150 rpm. At the end of the reaction, the flask was cooled, and the product was dissolved in chloroform and subsequently precipitated into methanol. The resulting solid was washed with methanol three times and dried under vacuum at 80 °C for 24 h. Bulk nanocomposites were labeled according to the concentrations of TiO2 nanowires as PLA/0.25% TiO2, PLA/0.5% TiO2, PLA/1% TiO2, and PLA/2% TiO2. Pure PLA without TiO2 nanowires was prepared following the same procedures and used as a control.

2.5. Isolation of PLA-g-TiO2 nanowires

The bulk nanocomposite is a mixture of free PLA and PLAGrafted TiO2 (PLA-g-TiO2) nanowires (Fig. 1). For characterization purposes, a repeated dispersion/centrifugation process was used to separate some PLA-g-TiO2 nanowires from free PLA in the bulk nanocomposite. Briefly, a portion of chloroform dispersed PLA/2% TiO2 nanowire bulk nanocomposite resulting from the previous step before precipitation into methanol was centrifuged at 8500 rpm for 30 min. The supernatant solution was precipitated into methanol to obtain free PLA. For the precipitant of PLA-g-TiO2 nanowires, the dispersion/centrifugation operation was performed repeatedly five times to ensure physically absorbed free polymers were completely removed. The PLA-g-TiO2 nanowires and free PLA were dried in a vacuum oven at 80 °C for 24 h to remove residual solvent and stored for future characterization.

2.6. Gel permeation chromatography (GPC) analysis

The weight- (Mw) and number-average molecular (Mn) weight as well as the molecular weight distribution (PDI, equals to Mw/Mn) were determined through GPC (Waters 2695 Separation Module). Samples were dissolved in chloroform. Because of the larger size of some TiO2 nanowires, all the solutions were filtered with 0.45 μm teflon filters before conducting GPC measurements. Measurement was performed at room temperature and a flow rate of 2 ml/min. The molecular weight was calibrated according to polystyrene standard.

2.7. Fourier-transform infrared (FTIR) spectroscopy

FTIR spectra were acquired with a PerkinElmer Spectrum 400 FT-IR/FT-NIR Spectrometer (Waltham, MA). Spectra were collected in the region of 4000–800 cm⁻¹ with a spectral resolution of 4 cm⁻¹ and 32 scans co-added.

2.8. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis

SEM (Hitachi S-3500N, Hitachi Science Systems, Ltd., Japan) and TEM (H-7100, Hitachi Co.) were used to study the morphology of the samples. For SEM, the samples were glued to aluminum specimen mounts, and the surface was coated with a mixture of 60% gold particles and 40% palladium with a sputter coater (Desk II Sputter/Etch Unit, NJ) before observation. For TEM, fine powders of each sample were absorbed onto Formvar/Carbon-coated 200-mesh copper grids (Electron Microscopy Sciences, Fort Washington, PA, USA) and observed without staining.

2.9. Differential scanning calorimetry (DSC) analysis

Thermal transitions were measured with a TA DSC Q200 instrument. About 5 mg of dried sample was sealed in a standard aluminum pan. An empty sealed pan was used as a reference. The sample was heated from 0 °C to 190 °C at a rate of 10 °C/min, isothermally conditioned at 190 °C for 3 min, quenched to 0 °C, isothermally conditioned at 0 °C for 3 min, and then heated again to 190 °C at the same rate. The sample was characterized in an inert environment by using nitrogen with a gas flow rate of 50 ml/min. Results were obtained from the second DSC heating scan except when otherwise specified. Heat capacity (∆Cp), melting temperature (Tm), cold crystallization temperature (Tc), melting temperature (Tm), heat of melting (∆Hm), and heat of crystallization (∆Hc) were determined from the DSC thermograms. The Tg was determined from the half width midpoint in the step change between the onset and the end temperatures of the transition. Crystallinity (Xm) was estimated according to the following equation:

\[ X_m(\%) = \frac{\Delta H_m}{\Delta H_0} \times X_{PLA} \times 100 \]

where \( \Delta H_m \) and \( \Delta H_0 \) are heats (J/g) of melting of PLA nanocomposites and of PLA crystals of infinite size with a value of 93.6 J/g [41], respectively, and \( X_{PLA} \) is the PLA fraction in the bulk nanocomposites.

2.10. Thermogravimetric analysis (TGA)

Decomposition characteristics of the samples were determined with a PerkinElmer Pyris1 TGA (Norwalk, CT). About 5 mg of each sample was placed in the pan and heated from 40 °C to 700 °C at a heating rate of 20 °C/min under a nitrogen or air atmosphere.

3. Results and discussion

3.1. Synthesized TiO2 nanowires

BET surface analysis gave a specific surface area of ~26.6 m²/g, average pore size of 12.1 nm, and pore volume of 0.081 cm³/g. Powder X-ray diffraction indicated that the TiO2 nanowires were dominated by anatase crystal structure. The UV–vis spectrum indicated that the TiO2 nanowires had a strong UV absorption ability with absorption peak at 294 nm (Fig. 2). The threshold of UV
absorption is $\sim 380$ nm, with the energy slightly higher than the bandgap of bulk anatase TiO$_2$ crystals ($\sim 388$ nm or 3.2 eV).

### 3.2. Molecular weight

Molecular weight and PDI of PLA and PLA/TiO$_2$ nanowire bulk nanocomposites are listed in Table 1. The $M_w$ and $M_n$ of pure PLA were 63,000 and 33,500, respectively, with PDI of 1.9. The $M_w$ of bulk nanocomposites with 0.25% TiO$_2$ nanowires was increased by 12% compared with pure PLA, with a broader PDI of 2.2. Similar molecular weight values to pure PLA were obtained for bulk nanocomposites with 0.5 and 1% TiO$_2$ nanowires. PLA/2% TiO$_2$ bulk nanocomposites showed significantly increased molecular weight, with $M_w$ and $M_n$ increased by 66 and 65%, respectively, compared with those of pure PLA. A similar increment of molecular weight was obtained for free PLA, which was isolated from PLA/2% TiO$_2$ bulk nanocomposites. As observed under TEM (not shown), quite a lot TiO$_2$ nanowires were noticed in free PLA, indicating that some TiO$_2$ nanowires were dispersed into chloroform during the centrifugation process. The increase of molecular weight might be explained by two reasons. First, although the nanocomposite solution was filtered with 0.45 μm teflon filter before GPC measurement, some nanowires could still pass the filter due to the significantly decreased size, as will be discussed in the morphology section, contributing to the higher molecular hydrodynamic volume. Second, the grafted PLA chains on the nanowire surface formed polymer brushes (Fig. 1), which also resulted in increased molecular weight.

### 3.3. FTIR

The FTIR spectra of PLA, pristine TiO$_2$ nanowires, PLA-g-TiO$_2$ nanowires, and PLA/2% TiO$_2$ nanowire bulk nanocomposites before isolating are presented in Fig. 3. The $M_w$ and $M_n$ of pure PLA were 63,000 and 33,500, respectively, with PDI of 1.9. The $M_w$ of bulk nanocomposites with 0.25% TiO$_2$ nanowires was increased by 12% compared with pure PLA, with a broader PDI of 2.2. Similar molecular weight values to pure PLA were obtained for bulk nanocomposites with 0.5 and 1% TiO$_2$ nanowires. PLA/2% TiO$_2$ bulk nanocomposites showed significantly increased molecular weight, with $M_w$ and $M_n$ increased by 66 and 65%, respectively, compared with those of pure PLA. A similar increment of molecular weight was obtained for free PLA, which was isolated from PLA/2% TiO$_2$ bulk nanocomposites. As observed under TEM (not shown), quite a lot TiO$_2$ nanowires were noticed in free PLA, indicating that some TiO$_2$ nanowires were dispersed into chloroform during the centrifugation process. The increase of molecular weight might be explained by two reasons. First, although the nanocomposite solution was filtered with 0.45 μm teflon filter before GPC measurement, some nanowires could still pass the filter due to the significantly decreased size, as will be discussed in the morphology section, contributing to the higher molecular hydrodynamic volume. Second, the grafted PLA chains on the nanowire surface formed polymer brushes (Fig. 1), which also resulted in increased molecular weight.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$</th>
<th>$M_n$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>63,000</td>
<td>33,500</td>
<td>1.9</td>
</tr>
<tr>
<td>PLA-0.25% TiO$_2$</td>
<td>63,300</td>
<td>37,500</td>
<td>2.2</td>
</tr>
<tr>
<td>PLA-0.5% TiO$_2$</td>
<td>66,800</td>
<td>34,500</td>
<td>1.9</td>
</tr>
<tr>
<td>PLA-1% TiO$_2$</td>
<td>66,100</td>
<td>31,300</td>
<td>2.1</td>
</tr>
<tr>
<td>PLA-2% TiO$_2$</td>
<td>104,800</td>
<td>55,200</td>
<td>1.9</td>
</tr>
<tr>
<td>Free PLA</td>
<td>104,300</td>
<td>59,200</td>
<td>1.8</td>
</tr>
</tbody>
</table>

* PDI - Molecular weight distribution ($M_w$/M_n).

### 3.4. Morphology

Fig. 4 illustrated the SEM micrographs of pristine TiO$_2$ nanowires and PLA-g-TiO$_2$ nanowires. The pristine nanowires exhibited quite clean surface. The diameter was $\sim 50$–$200$ nm and length from a few micrometers to $\sim 20$ μm (Fig. 4A), which is consistent with the literature [39]. The pristine nanowires were aggregated but were still discernible as single wires at higher magnification. Such nanowires were easily dispersed into lactic acid monomer homogeneously at the beginning of polymerization. Appreciable differences in morphology and size were observed between PLA-g-TiO$_2$ nanowires and pristine TiO$_2$ nanowires (Fig. 4B). In contrast to the pristine TiO$_2$ nanowires, PLA-g-TiO$_2$ nanowires seemed much thicker, but still kept the wire-like structure. The length of PLA-g-TiO$_2$ nanowires was also reduced significantly, compared with pristine nanowires. The nanowires are fragile, and they were broken down during the polymerization processes. Decreased length of TiO$_2$ nanofibers was also reported by Khaled et al. [32] when polymerizing methyl methacrylate monomers onto the surface of TiO$_2$ nanofibers in synthesizing poly(methyl methacrylate)/TiO$_2$ nanocomposites.

As an additional evidence for the existence of PLA chains on nanowire surface, analysis of TEM was conducted and the typical results are shown in Fig. 5. Similar to SEM, significant reduction of size was also noticed for PLA-g-TiO$_2$ nanowires under TEM, compared with that of pristine TiO$_2$ nanowires (Fig. 5A and B). The individual TiO$_2$ nanowires before and after surface grafting were clearly observed at higher magnification (Fig. 5A’ and B’). The surface of pristine TiO$_2$ nanowires seemed to be smooth and clear without any extra phase adhering to them (Fig. 5A’). In contrast, the PLA-g-TiO$_2$ nanowires shown in Fig. 5B’ appeared stained with extra phase (dark area on the nanowire surface) that is presumed to come from grafted PLA molecules.

The SEM micrographs of PLA and bulk nanocomposites are presented in Fig. 6. The surface of pure PLA was quite flat and smooth (Fig. 6A). As the concentration of TiO$_2$ nanowires increased,
much more coarse and uneven surfaces were observed for the bulk nanocomposites (Fig. 6b–e). The nanowires were not discernible from the surface morphology by SEM imaging. We did not observe any phase separation in the bulk nanocomposites. In general, chemical grafting of polymer chains that are compatible with the polymer matrix on the inorganic nanoparticles provides strong interfacial interaction between the inorganic and the organic phases [43].

TEM is a powerful tool for studying the dispersion of nanoparticles embedded within a polymer matrix. The typical TEM micrographs of PLA and bulk nanocomposites are shown in Fig. 7. No nanowire aggregation was observed in the polymer matrix. The individual nanowires appeared to be distributed homogeneously throughout the polymer matrix (Fig. 7c'). At higher magnification, we observed that the nanowire surface was covered with a third phase due to the presence of PLA (inserted image of Fig. 7c'). TEM
images indicated that the distinct phase on TiO\textsubscript{2} nanowire surfaces prevented the hydrophilic aggregation of pristine nanowires and resulted in a better dispersion of nanowires. The surface grafting could also improve the hydrophobic entanglements of grafted PLA chains with surrounding free PLA matrix.

3.5. Thermal properties

DSC thermograms showing the $T_g$ of pure PLA and PLA-g-TiO\textsubscript{2} nanowires are presented in Fig. 8. The $T_g$ was determined from the half width midpoint between the onset and the end temperatures of the transition, as indicated by the dash lines in the thermograms. About a 7 °C increment of $T_g$ was observed for those PLA chains grafted onto TiO\textsubscript{2} nanowire surface compared with pure PLA, as obtained from the first DSC heating scan (Fig. 8A). After erasing the thermal history, although the $T_g$ of both PLA and PLA-g-TiO\textsubscript{2} nanowires decreased due to the loss of the chain conformational ordering, $T_g$ of the latter was still 6 °C higher (Fig. 8B). The very small heat capacity change at the glass transition for PLA-g-TiO\textsubscript{2} nanowires was probably because of the low PLA ratios (≈30%) in the sample and relatively short grafted PLA chains. The increased $T_g$ sustained the evidence that strong bonding existed between the grafted PLA chains and TiO\textsubscript{2} nanowires, which led to permanent attachment of PLA chain segments onto the TiO\textsubscript{2} nanowire surface. The increased $T_g$ was caused by the restrictions on the mobility of chains in the vicinity of the surface \[44\]. The reduction of chain mobility was possibly caused by crowding and/or local ordering of chains at the interface as well as loss of configurational entropy of the PLA segments near the nanowire surface \[45\]. Molecular dynamics simulations also showed that the relaxations of chain segments in the immediate vicinity of the nanoparticles were slower \[46\].

Fig. 9 shows the DSC thermograms of PLA/TiO\textsubscript{2} nanowire bulk nanocomposites, and quantified results are summarized in Table 2. All the thermograms were obtained from the second DSC heating scan after erasing the thermal history, and they
exhibited three thermal transitions, i.e., glass transition, cold crystallization, and melting of PLA. Pure PLA showed a $T_g$ of 54.7 °C, while the bulk nanocomposites exhibited elevated $T_g$ as the TiO$_2$ nanowire concentrations were increased from 0 to 2%. Maximum $T_g$ was obtained for PLA/2% TiO$_2$ nanowire bulk nanocomposites, which was 4 °C higher than that of pure PLA.

As discussed before, the permanent graft of PLA chains onto the nanowire surface leads to restricted mobility of chain segments; therefore, $T_g$ increased. With higher concentrations of nanowires in bulk nanocomposites, more grafted chain segments onto nanowire surface were expected, leading to larger $T_g$.

**Fig. 7.** Typical TEM micrographs of PLA and PLA/TiO$_2$ nanowire bulk nanocomposites (a/a', PLA; c/c', PLA/0.5% TiO$_2$; scale bar: left, 2 μm; right, 200 nm).

**Fig. 8.** DSC thermograms of PLA and PLA-g-TiO$_2$ nanowires (A, first heating scan; B, second heating scan).
The $T_c$ and $T_m$ of pure PLA was 110 and 153/160 °C, respectively, with crystallinity of 47%. Decreased crystallinity was observed for all the bulk nanocomposites with TiO2 nanowires. Bulk nanocomposites with 0.5 and 2% nanowires exhibited lowest crystallinity. More than a 10 °C increment of $T_c$ was observed for these two bulk nanocomposites, implying their lowest crystallization ability. These phenomena were probably caused by the reduction of the diffusion of the PLA chains to the growing crystalline lamella and disruption of the regularity of the chain structures in PLA in the presence of TiO2 nanowires. The incontinuous decrease of crystallinity with increasing nanowire loadings might be related with an inhomogeneous dispersion of TiO2 nanowires in samples with the lowest crystallinity, and improved nanowire dispersion for the other ones. PLA and bulk nanocomposites with less than 1% TiO2 nanowires exhibited double melting behaviors, which were caused by the separate melting of the PLA crystals with low structural perfection and normal PLA crystals and the melting-recrystallization to the higher perfection-remelting process of PLA crystals [47,48]. Decreased $T_m$ was obtained for bulk nanocomposites with increased concentration of TiO2 nanowires. Double melting peaks merged into one single peak at 149 °C for PLA/2% TiO2 nanowire bulk nanocomposites, indicating the difficulties in forming PLA crystals with higher perfection at high concentration of nanowires, which might be caused be the presence of more grafted PLA chains.

The TGA thermograms of intensively dried PLA, pristine TiO2 nanowires, and PLA-g-TiO2 nanowires were presented in Fig. 10. These thermograms were obtained under air atmosphere to quantitatively estimate the grafting ratio of organic PLA chains on the TiO2 nanowire surface. The weight loss of TiO2 nanowires and PLA-g-TiO2 nanowires were 9 and 40% respectively, after achieving the thermogram plateaus during heating. Based on the differences of weight loss between TiO2 nanowires before and after surface grafting, more than 30% PLA in weight were certainly grafted onto nanowire surface. The grafted PLA chains exhibited two-stage thermal decomposition behaviors. The first decomposition occurred at the peak temperature of 308 °C, which was related to the polymer chains far away from the nanowire surfaces. The first decomposition temperature was slightly higher than that of pure PLA (300 °C). The second decomposition occurred at the peak temperature of 560 °C, which was probably caused by the polymer chains in the vicinity of the nanowires. Similar increments of thermal decomposition temperatures were also reported for in situ polymerized poly(3-hexylthiophene) grafted TiO2 nanotube nanocomposite and polystyrene grafted TiO2 nanocomposite [33,49]. The dramatically increased thermal decomposition temperature of those grafted PLA chains was probably caused by its different

<table>
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<tr>
<th>Sample</th>
<th>$T_g$ °C</th>
<th>$\Delta C_p$ J/(g·°C)</th>
<th>$T_c$ °C</th>
<th>$\Delta H_{cc}$ J/g</th>
<th>$T_m$ °C</th>
<th>$\Delta H_{mm}$ J/g</th>
<th>$X_m$ %</th>
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<td>43.1</td>
<td>152.7</td>
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structure once covalently bonded to nanowire surface and restricted thermal motion of the chains in the gallery [50].

The thermal stability of PLA and bulk nanocomposites with TiO2 nanowires was studied via TGA under an inert nitrogen atmosphere. The TGA thermograms are shown in Fig. 11, and the thermal decomposition temperatures of PLA and bulk nanocomposites containing TiO2 nanowires derived from TGA thermograms.

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>T\textsubscript{max} °C</th>
<th>T\textsubscript{onset} °C</th>
<th>T\textsubscript{end} °C</th>
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<td>PLA</td>
<td>276.2</td>
<td>308.3</td>
<td>296.6</td>
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<tr>
<td>PLA-0.25 TiO\textsubscript{2}</td>
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<td>306.4</td>
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<td>PLA-2% TiO\textsubscript{2}</td>
<td>274.5</td>
<td>322.6</td>
<td>302.3</td>
</tr>
</tbody>
</table>

4. Conclusions

Bionanocomposites with covalent bonding between TiO2 nanowire surface and PLA chains were synthesized through in situ melt polycondensation. The covalent grafting of PLA chains onto the nanowire surfaces was confirmed by FTIR spectroscopy and TGA. TEM micrographs and DSC results also supported the presence of the third phase on the nanowire surfaces. Those PLA on the nanowire surfaces exhibited significantly increased T\textsubscript{g} and thermal stability, compared with pure PLA. TGA results also showed that more than 30% of PLA in weight were certainly grafted onto the nanowire surfaces. Increased molecular weight was obtained for PLA/2% TiO\textsubscript{2} nanowire bulk nanocomposites, of which the M\textsubscript{w} was 66% higher than that of pure PLA. TEM micrographs indicated that homogeneous dispersion of TiO\textsubscript{2} nanowires in the PLA matrix was achieved. The T\textsubscript{g} of bulk nanocomposites increased, whereas the crystallization ability decreased, as the nanowire concentrations increased from 0 to 2%.

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