Crystallization Behavior of Poly(lactic acid)/Titanium Dioxide Nanocomposites

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Abstract

In this study, a poly(lactic acid) (PLA) with various titanium dioxide (TiO_2) nanoparticles loading were prepared by a manual laboratory mixing method. The effect of TiO_2 nanoparticles on the non-isothermal and the isothermal crystallization behavior of PLA was investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The presence of TiO_2 nanoparticles decreased the spherulite growth rate of PLA, whereas it initiated faster crystallization through the heterogeneous nucleation process as observed by optical microscopy. The results of DSC analyzes confirmed that the TiO_2 nanoparticles act as an efficient nucleating agent for PLA crystallization. The cold crystallization temperature and crystallization half-time of PLA decreased, while the degree of crystallinity of PLA increased in relation to increases of TiO_2 nanoparticles.

Keywords: Poly(lactic acid), Titanium dioxide, Nanocomposites, Crystallization

1 Introduction

Poly(lactic acid) (PLA) has attracted increasing interest as a substitution for petroleum-based plastics due to its biodegradability, high strength, and high modulus properties. However, it's inherent brittleness and slow crystallization rate has limited its large scale commercial application [1]. Normally, the slow crystallization rate causes difficulties in the ejection of parts and results in longer molding cycles in the injection molding process. Therefore, an increase in the crystallization rate of the PLA becomes a concern for extending PLA into various industrial applications (electronics, automotive parts, etc.).

Considering that PLA is a semi-crystalline polymer, its overall properties are governed by the morphological structure of the polymer, which is controlled by the respective crystallization process during production [2]. Generally, crystallization process occurs in two stages, which are nucleation and growth. These two processes occur independently of each other. In the nucleation step, the randomly tangled molecules in a polymer melt align and form small ordered regions, which are called nuclei. The formation of nuclei is highly dependent on the degree of supercooling. This degree of supercooling is defined as the difference between the equilibrium melting temperature and the crystallization temperature of a semi-crystalline polymer [3]. However, impurities such as organic or inorganic additives can act as nuclei also.

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The crystallization, i.e. the locally parallel arrangement of polymer chains in the so-called crystal lamellae, starts on these nuclei. Aggregates of crystalline lamellae finally most frequently appear in a spherulitic scape. This arrangement is called "Supermolecular Structure" [4].

The change of spherulite radius during crystallization at a given crystallization temperature is usually linear with time and is called growth rate. It is known that the spherulite growth rate strongly depends on crystallization temperature and the molecular weight of the polymer [5]. Finally, the growth of spherulites stops when the impingement of neighboring spherulites occurs.

Actually, the incorporation of a nucleating agent is one of the most effective methods to overcome the slow crystallization rate of polymer and is widely used in the plastics industry. Nucleating agents can help to increase the nuclei density in the nucleation process and finally reduce the spherulite size, resulting in an improvement of the overall crystallization rate of the polymer in processing. Therefore, many considerable interests have focused on accelerating polymer crystallization with nano-filler, e.g. talc [6], organoclays [7], cellulose nanocrystals [8], carbon nanotubes [2], [9], [10], and titanium dioxide (TiO_2) [11], [12]. However, there is almost no literature that reports on the approach to improve the crystallization process of PLA by the incorporation of TiO_2 nanoparticles.

In this article, the effect of TiO_2 nanoparticles loading on the PLA crystallization behavior was investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC).

2 Experimental and Characterization

2.1 *Materials*

Poly(lactic acid) (PLA) (NatureWorks LCC, grade 4042D (95.8% L-lactide and 4.2% D-lactide)) was used for this study. The number average molecular mass, Mn and density of the PLA are 183,000 g/mol and 1.25 g/cm^3, respectively [13]. As nano-sized filler titanium dioxide nanoparticles (TiO_2) (Huntsman International LLC, Hombitec RM 130 F) were used. These nanoparticles exhibit an acicular form and have a mean diameter of about 15 nm according to the manufacturer.

2.2 *PLA/TiO_2 nanocomposites preparation*

The films of PLA and PLA/TiO_2 nanocomposites with 0, 1, 2 and 4 vol.% of TiO_2 nanoparticles were prepared by a simple manual mixing method as described in [14].

2.3 *Characterization*

2.3.1 Optical Microscopy (OM)

A small piece of material was cut from the PLA and PLA/TiO_2 nanocomposites thin films, which has been prepared according to 2.2. The pieces were applied onto a glass slide and covered with a cover slip. Then, it was re-molten, compressed, and quenched on the hot plate to get finally a film thickness of about 25/±5 μm. Then the materials were analyzed by using a hot stage (LTS 520, Linkam Scientific Instruments, Surrey) under a Polarized Optical Microscope (ECLIPSE LV100, Nikon GmbH, Düsseldorf), attached to a video recording system (Nikon Digital Sight DS-U3).

For the non-isothermal crystallization studies, the material was heated from room temperature to 200°C, with a heating rate of 10 K/min, and held at that temperature for 3 min to remove thermal history. Then, the material was cooled down to room temperature with a rate of 5 K/min.

The spherulite growth rate was obtained from isothermal crystallization studies. The material was heated from room temperature to 200°C with a heating rate of 20 K/min, and held at that temperature for 3 min. Then, the sample was cooled down with a cooling rate of 20 K/min to various given isothermal crystallization temperatures (105–130°C) and held constant until completion of crystallization was observed. The measurements of the spherulite radius (R) as a function of time (t) were performed on five different spherulites per experiment. Then, the spherulite growth rate (dR/dt) was calculated as the slope of the line fitted to the experimental data at a given crystallization temperature.

Each crystallization experiment was performed at least 3 times in order to verify the reproducibility of the experiment.

2.3.2 Differential Scanning Calorimetry (DSC)

The thermal properties were determined using DSC (TA Q20, TA instruments, Eschborn). An indium was used as a reference material to calibrate both the temperature scale and the melting enthalpy. The nitrogen gas was purged throughout the measurement. The weight of each specimen was always 5 to 10 mg. The specimen was placed in an aluminum pan and then was completely sealed with an aluminum lid. The material was heated up from 0°C to 200°C at a heating rate of 10 K/min, and then held at this temperature for 3 minutes to remove the thermal history. Then, for non-isothermal crystallization the material was then cooled from 200°C to 0°C at a cooling rate of 5 K/min. The glass transition temperature T_g, cold crystallization temperature, T_{cc} (determined at the peak of exothermic crystallization area) and melting temperature, T_m (determined at the peak of endothermic melting area). The degree of crystallinity, X, was calculated using the following equation,

$$\%X = (\Delta H / \Delta H^{\circ}_{m} w_{PLA}) \times 100 \tag{1}$$

where $\Delta H = \Delta H_m - \Delta H_{cc}$, as ΔH_m is the melting enthalpy of the specimen and ΔH_{cc} is the cold crystallization enthalpy of the specimen, ΔH°_{m} is the melting enthalpy of a theoretically 100% crystalline PLA (93 J/g) [15], and w_{PLA} is the mass fraction of PLA in the composite.

For isothermal crystallization, the material was quenched to various isothermal crystallization temperatures, T_i within the range of 110°C to 125°C at a cooling rate of 40 K/min, and kept constant at that temperature until the crystallization was completed. The heat evolved during the isothermal crystallization (H_c) was recorded as a function of time. The time required for each isothermal crystallization conditioning depended on the value that had been chosen for T_i. To minimize thermal degradation, each specimen was used only one time.

3 Results and Discussion

3.1 *Polarized optical microscopy observations*

3.1.1 Non-isothermal crystallization

In fact, the crystallization of neat PLA is very difficult to occur from the melt in the non-isothermal quenching process [2]. In our experiments, a formation of a supermolecular morphology during the cooling process was not observed. However, during a second heating spherulite growth was clearly visible. Therefore, the polarized optical micrographs are taken during non-isothermal cold crystallization (during the second heating process). Figure 1 shows the development of the spherulite structure of PLA and its nanocomposites. In the optical (2-dimensional) micrographs, the spherulites appear as discs with blue and orange colors, whereas the dark spots represent the TiO_2 nanoparticles and their agglomerates. It can be observed that neat PLA presents a clean and uniform melt, while micro-scale agglomerates of TiO_2 nanoparticles were found in the PLA nanocomposites. The spherulites are visible at about 115°C in the case of PLA nanocomposites, whereas in case of neat PLA is still fully molten. Moreover, it can be seen that as the TiO_2 content increased, a progressively higher number of spherulites

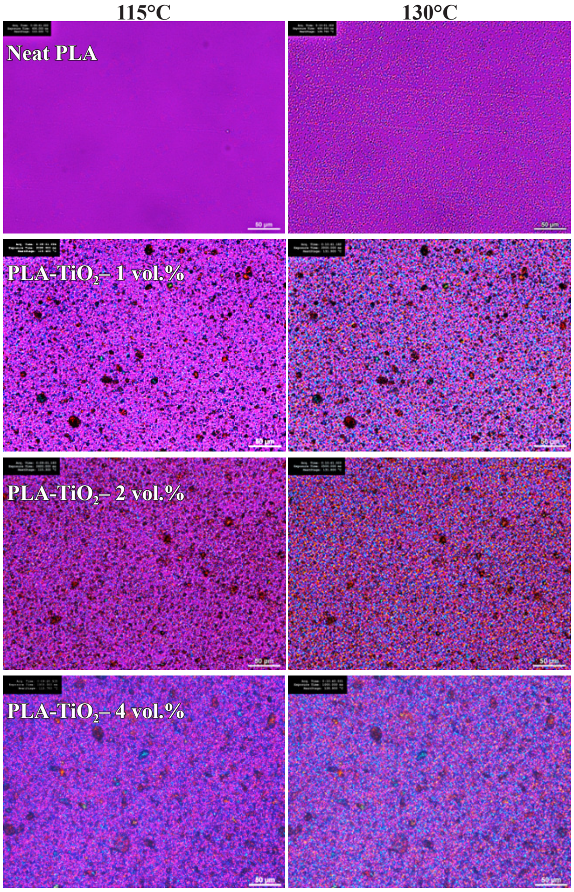


Figure 1: The optical micrographs of the spherulites of PLA with different TiO_2 loadings obtained from non-isothermal cold crystallization during the second heating process at 115°C and 130°C (Scale bar, 50 μm).

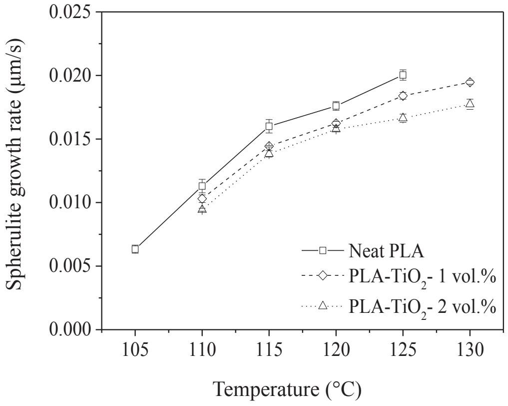


Figure 2: The spherulite growth rate of neat PLA and its nanocomposites with different TiO_2 nanoparticles loading at various crystallization temperatures.

formed at the given temperature. The growth of spherulites occurs in all cases at a temperature of about 130°C. Furthermore, it was found that the higher the content of the nanoparticles, the larger area covered by spherulites taken at the same temperature. This result indicates that the TiO_2 nanoparticles facilitate faster overall crystallization in PLA [8], [10].

3.1.2 Isothermal crystallization

The spherulite growth rate of the materials was obtained from isothermal crystallization studies. Figure 2 shows the spherulite growth rate of neat PLA and its nanocomposites with different TiO_2 nanoparticles loading at various crystallization temperatures. Because of a very slow crystallization rate of neat PLA, the crystallization temperatures above 125°C were not examined in this work for neat PLA. Moreover, in the case of PLA filled with 4 vol.% TiO_2 and the case of crystallization temperatures below 110°C are not possible for measurements of the spherulite growth rate because of the very high nucleation density. From Figure 2, as expected, the spherulite growth rate increases with increasing crystallization temperatures for both neat PLA and PLA nanocomposites. This can be explained by the increase in polymer chain mobility for the folding process at a higher temperature [5]. Nevertheless, the spherulite growth rate of PLA slightly decreases with the addition of 1 vol.% of TiO_2 nanoparticles, and decreases continuously with increasing TiO_2 nanoparticle content from 1 to 2 vol.% as seen in Figure 2. This may be due to the restriction of chain mobility of PLA by the nanoparticles during the crystallization process [16].

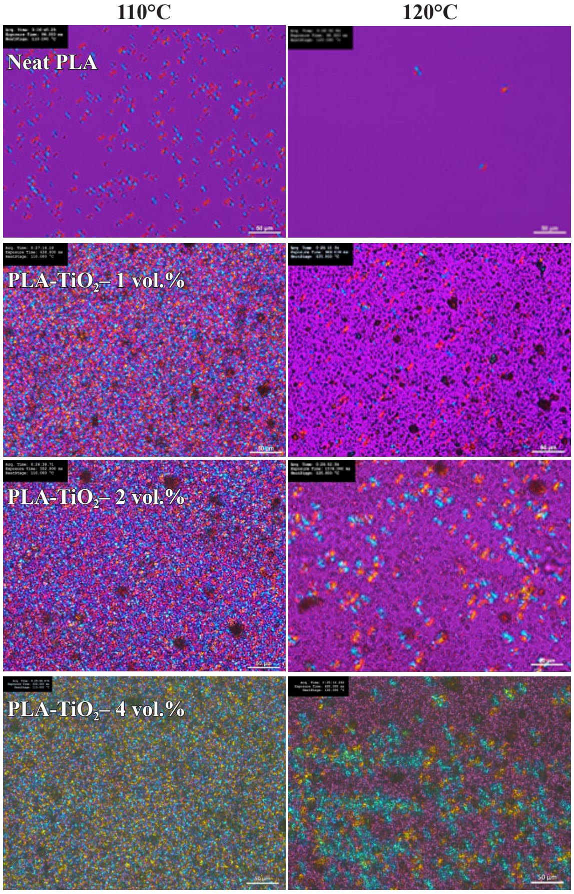


Figure 3: The optical micrographs of the spherulites of PLA with different TiO_2 loadings obtained from isothermal crystallization at temperature 110°C and 120°C with crystallization time 10 minutes (Scale bar, 50 μm).

The optical micrographs of PLA and its nanocomposites during isothermal crystallization at 110°C and 120°C are shown in Figure 3. As expected, the number of spherulites depends directly on the crystallization temperature. The amount of the spherulites of neat PLA decreases with increasing crystallization temperature. This is attributed to the fact that the formation of nuclei depends on the degree of supercooling [3]. At high degrees of supercooling (low crystallization temperature), a high amount of spherulites of neat PLA is observed. In contrast, when the degree of supercooling is decreased (high crystallization temperature), a small number of spherulites is obtained. Thus, the spherulites size apparently increases with an increase of crystallization temperature due to the decrease in spherulite density.

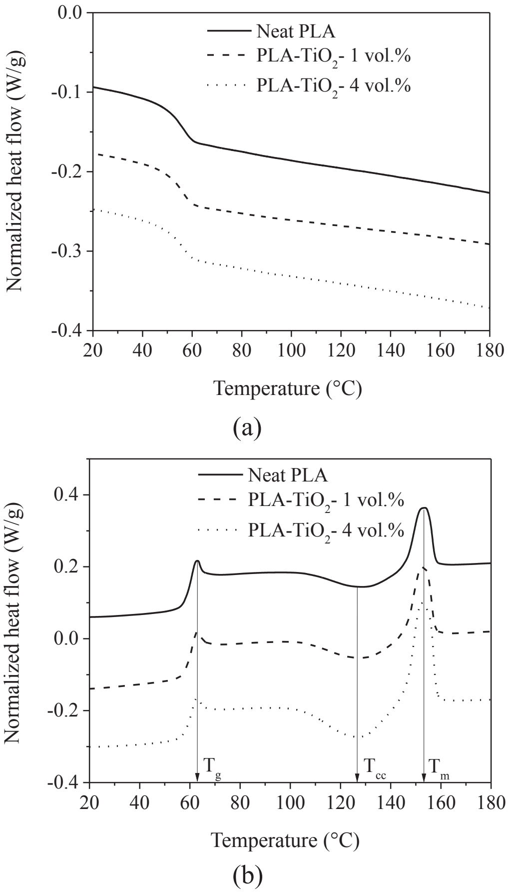
Moreover, it was interesting to note that the addition of TiO_2 nanoparticles greatly changes the supermolecular morphology of PLA. With the presence of TiO_2 nanoparticles, the large number of spherulites is induced within a short time. With increases in TiO_2 nanoparticle loading, the amount of spherulites of PLA/TiO_2 nanocomposites continuously increases. This observation indicates that the TiO_2 nanoparticles act as a heterogeneous nucleating agent, assisting the crystallization of the PLA nanocomposites. Therefore, the overall crystallization rate of PLA/TiO_2 nanocomposites increases indicating by the larger area covered by the spherulites taken at the same crystallization time. Additionally, the spherulite size of PLA/TiO_2 nanocomposites seems smaller than that of neat PLA. With increasing TiO_2 nanoparticle loading, the spherulite size of PLA/TiO_2 nanocomposites gradually decreased. This is due to the increase of the nucleation density of PLA/TiO_2 nanocomposites. The higher nucleation density provides faster solidification, which can cause advantages in the processing of the final part due to potentially shorter cycle times.

It is well known that the overall crystallization rate is a result of the appearance of the nucleation rate and the growth rate. The above results on the growth rate of materials show that the growth rate decreases with increasing the TiO_2 nanoparticles loading, whereas the nucleating rate seemingly increases with increasing the TiO_2 nanoparticles loading. However, the optical micrograph results indicate that the TiO_2 nanoparticles enhance the overall crystallization process of the PLA. These results suggest that the nucleating rate is a dominant process that controls the overall crystallization rate of PLA in this work which can help to reduce the cycle time in the injection process.

3.2 *Differential scanning calorimetry analysis*

3.2.1 Non-isothermal crystallization

The DSC thermograms recorded during the first cooling and second heating of the neat PLA and PLA/TiO_2 nanocomposites are presented respectively in Figure 4 (a) and (b). It can be seen that both neat PLA and PLA/TiO_2 nanocomposites do not crystallize during cooling. The crystallization of all materials occurs during second heating (cold crystallization, see Figure 4 (b)). The results derived from second heating thermograms are listed in Table 1. As shown, the T_g and T_m of PLA/TiO_2 nanocomposites slightly decrease compared to the neat PLA. It is known that lower T_{cc} initiates faster crystallization. In this work, the exothermic peak of cold crystallization of neat PLA is found at 130.2°C. The incorporation of TiO_2 slightly decreases the T_{cc}, with a T_{cc} of 129.5°C for PLA-TiO_2 -1 vol.% and 128.2°C for PLA-TiO_2 -4 vol.%. This implies that TiO_2 nanoparticles can be a nucleating agent for PLA.



(a)

(b)

Figure 4: DSC thermograms of PLA with different TiO_2 loadings obtained from first cooling run (a) and second heating run (b).

Table 1: DSC second heating results of PLA with different TiO_2 loadings

Material	T_g, °C	T_{cc}, °C	T_m, °C	X_m, %	X_{cc}, %	X_m -X_{cc}, %
Neat PLA	60.9	130.2	153.5	7.3	6.5	0.8
PLA-TiO_2 -1 vol.%	61.1	129.5	153.4	9.0	9.0	0.3
PLA-TiO_2 -4 vol.%	59.5	128.2	152.8	16.9	16.7	0.3

Although the crystallization of PLA is not detected during cooling, the PLA crystals are formed partially during this stage. However, the crystallinity formed during the cooling of all materials is very low, ranging from 0.3 to 0.8% (evaluated as X_m -X_{cc}), whereas the crystallinity formed during heating (X_{cc}) increases from 6.5 to 16.7% with increased TiO_2 loading. Consequently, the total crystallinity, X_m, of neat PLA with respect to a combination of the crystallinity formed during cooling and heating significant increases with increases of TiO_2 loading.

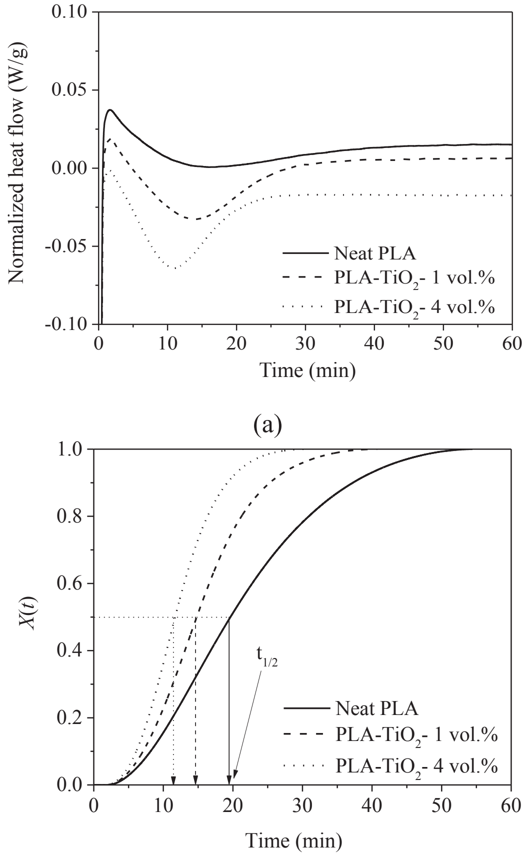
3.2.2 Isothermal crystallization

Figure 5 (a) shows the exothermal crystallization of neat PLA and PLA/TiO_2 nanocomposites at the isothermal temperature (T_i) of 110°C. With increasing TiO_2 loading the exothermic crystallization shifts towards shorter time and becomes narrower. This means that the time required to complete the crystallization is shorter and that the crystallization rate is faster when the TiO_2 loading is higher.

Investigation on isothermal crystallization kinetics is usually carried out using data obtained from exothermic crystallization. This is based on the assumption that the evolution of crystallinity is directly proportional to the heat evolved during the progress of crystallization [17]. By integrating the heat evolved during crystallization, the relative degree of crystallinity as a function of crystallization time *X*(*t*) can be defined as follows,

$$X(t) = \frac{Q_t}{Q_\infty} = \int_0^t \frac{dH}{dt}dt \int_0^\infty \frac{dH}{dt}dt \qquad (2)$$

where Q_t and Q_∞ are the heat generated at time t and at an infinite time t_∞, respectively. *dH* is the heat evolution of crystallization during an infinitesimal time interval *dt*.



(a)

(b)

Figure 5: Typical crystallization exothermic curve (a) and relative crystallinity, *X*(*t*) as a function of crystallization time (b) of PLA with different TiO_2 loadings, T_i = 110°C.

The typical S-shape of *X*(*t*) for neat PLA and PLA/TiO_2 nanocomposites, which was calculated by integration of the exothermic crystallization traces (Figure 5 (a)) according to equation (2), is shown in Figure 5 (b). As we can see, the time to reach the ultimate crystallinity decreases with increasing TiO_2 loading. From this S-shape of *X*(*t*), the half-time of crystallization ($t_{1/2}$) defined as the time spent from the beginning of the crystallization to the completion of half of the final crystallization can be measured directly. The inverse of the half-time of crystallization ($1/t_{1/2}$) is referred to the overall of crystallization rate [18]. A higher value of $t_{1/2}$ indicates a slower crystallization rate, and vice versa. The $t_{1/2}$ values of the materials as a function of the TiO_2 loading and the T_i are shown in Table 2.

Table 2: Half-time of the isothermal crystallization ($t_{1/2}$) for PLA with different TiO_2 loadings at various temperatures, the unit of $t_{1/2}$ is given in minutes (min)

T_i, °C	110	115	120	125
Neat PLA	19.6	25.7	68.0	121.8
PLA-TiO_2 -1 vol.%	14.8	22.2	57.5	117.0
PLA-TiO_2 -4 vol.%	11.7	21.5	49.9	113.4

In Table 2, the $t_{1/2}$ increases as the T_i increased for all materials. At the same T_i the addition of TiO_2 reduces the $t_{1/2}$. Higher TiO_2 loading results in lower $t_{1/2}$. This indicates that TiO_2 nanoparticles can act as nucleating agent for PLA, the higher the TiO_2 loading the higher nucleating site, thus the higher the crystallization rate of PLA.

4 Conclusions

Basically, the presented studies show that nanoscale TiO_2 under isothermal conditions certainly acts as a nucleating agent in PLA. However, non-isothermal crystallization investigations with hot stage optical microscopy and DSC studies show that even at moderate cooling rates of 5 K/min TiO_2 is not able to trigger the crystallization noticeably. Only a second heating of the material results in a post-crystallization at roughly 50°C above T_g.

The isothermal investigations both in the optical microscope and in the DSC show clearly that the heterogeneous nucleation by TiO_2 particles determines the crystallization process. A higher proportion of TiO_2 basically leads to smaller spherulites, but also to a slower spherulite growth rate. The thermoanalytical investigations show that the TiO_2 addition slightly reduces the glass transition temperature, the temperature for cold-crystallization temperature and the melting temperature as well. By contrast, the degree of crystallinity increases by the addition of nanoparticles.

Overall, it can be concluded that TiO_2 one hand acts as a nucleating agent, on the other hand also impede crystallization from the melt. This results in smaller spherulites with also lower degree crystallinity in the volume after processing. However, due to a second heating (still far below the melting temperature) and therefore cold crystallization, the decree of crystallinity of PLA/TiO_2-nanocomposites finally exhibits a threefold of the value of non-filled PLA. The weakness of PLA expressed by a low degree of crystallinity after processing and even after cold crystallization can therefore partially be eliminated by the addition of nanosized TiO_2.

The findings can be used in practice in the crystallization of PLA granules in processes prior to molding. A shortening of the cold crystallization time by up to 40% can significantly reduce the costs in the production of PLA-molded parts.

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