ISSN 2616-5880 Vol. 4, Issue 7: 83-88, DOI: 10.25236/AJMC.2023.040713

Study on Preparation, Properties, and Degradation Behavior of Nano-Tio_2/PolyLactic Acid Composites

Dan Chen[1,a,*], Jun Shao[1,b], Zhengrong Xu[2,c]

[1]Taizhou Vocational College of Science & Technology, Taizhou, Zhejiang, 318020, China
[2]Taizhou Jurong Plastics Co., LTD, Taizhou, Zhejiang, 318020, China
[a]chend@tzvcst.edu.cn, [b]shaoj@tzvcst.edu.cn, [c]xuzhengrong@jurongsuhua.com
[*]Corresponding author

Abstract: *As a semiconductor material, nano TiO_2 has important application value in various professional fields. Single nano TiO_2 has low light utilization and poor degradability. In order to improve the sustainability of material development, enhance the application value and performance of materials, this article combined polylactic acid (PLA) with nano TiO_2 to form a composite material, and studied its preparation, characterization, and degradation behavior. This article first analyzed the characteristics of nano TiO_2 and polylactic acid materials, then prepared and modified nano TiO_2, and finally combined it with different mass ratios of polylactic acid to form composite material samples. To verify the material performance, this article conducted experiments from two aspects: characterization of crystallization performance and analysis of degradability. The results showed that the higher the PLA mass ratio, the more ideal the degradability of the composite material. Compared to the material with a PLA mass ratio of 0%, the degradability of the material sample with a PLA mass ratio of 3% ultimately increased by 0.12%. The conclusion indicates that the polylactic acid nano TiO_2 composite material has excellent degradability, which helps to improve the environmental friendliness and application range of the material.*

Keywords: *Polylactic Acid, Nano Titanium Dioxide, Material Degradation, Performance Characterization, Preparation of Composite Materials*

1. Introduction

With the continuous development of the social economy, environmental and energy issues are becoming increasingly prominent, and the development and preparation of environmentally friendly materials is becoming increasingly important for the sustainable development of the manufacturing industry. Nano TiO_2 has excellent photocatalytic performance and has important value and prospects in fields such as environmental pollution control. However, in practical applications, a single nano TiO_2 has low biodegradability and is difficult to achieve effective recovery, which limits its application range to a certain extent.

Polylactic acid is a biodegradable polymer material with good biocompatibility and degradability. It can serve as a carrier to effectively wrap nano TiO_2 inside, improve material recovery, promote the decomposition of degradation products generated by photocatalytic reactions, and thereby improve material degradation efficiency and stability of degradation products. Combining it with nano TiO_2 to form composite materials has important practical value for environmental protection and sustainable development.

In order to effectively improve material performance and sustainable use value, this article conducted in-depth research on the preparation, characterization, and degradation behavior of polylactic acid nano TiO_2 composite materials. To verify the performance and effectiveness of the prepared composite material samples, this article classified the materials according to the PLA mass ratio, and verified them from two aspects: material crystallization performance and degradability. In terms of crystallization performance, the higher the mass ratio of PLA, the smaller the diffraction peak width of the material, and the more regular its crystal structure. In terms of degradability, compared with materials with a PLA mass ratio of 0%, the degradability of materials with a PLA mass ratio of 3% ultimately increased by 0.12%. In practical applications, the composite material composed of PLA and nano TiO_2 has stronger photocatalytic and degradable properties.

ISSN 2616-5880 Vol. 4, Issue 7: 83-88, DOI: 10.25236/AJMC.2023.040713

With the rapid development and application of new technologies such as optoelectronics and remote sensing, monitoring of karst collapse terrain changes on highways has also achieved certain results. Chi Hai studied the microstructure, thermal properties, mechanical properties, oxygen and water resistance of PLA/nano TiO_2 composite membranes before and after high-pressure treatment. Through analysis of the barrier performance, it was found that the barrier performance of the composite membrane after high-pressure treatment was improved [1]. Tajdari Ali synthesized PLA/TiO_2 nanocomposites using hydrothermal method and studied their microstructure, optical, mechanical, hydrolytic degradation, and antibacterial properties. He observed that the aggregation trend of the combined nanoparticles increased significantly [2]. Zhang Zheng prepared PLA/TiO_2 PDA nanocomposites by compounding polydopamine (PDA) with PLA. Finally, through performance characterization, it was found that the prepared compliant material film has a wider range of applications and longer service life in environmentally friendly materials [3]. Liao Chenggang blended different particle sizes of nano TiO_2 with molten PLA to modify wheat straw fibers, resulting in a composite material modified with nano TiO_2. Mechanism studies have shown that nano TiO_2 enhances the interfacial compatibility of composite materials by promoting heterogeneous nucleation and rapid crystallization of polylactic acid [4]. Hou Xuebin deposited TiO_2 nanoparticles on the porous electrospun PLA fiber substrate, and compared with powdered TiO_2, the composite fibers loaded with TiO_2 exhibited significant photocatalytic activity [5]. Athanasoulia Ioanna-Georgia investigated the effects of incorporating TiO_2 nanoparticles through extrusion melt blending on the various characteristics and properties of low crystallinity poly (L-lactic acid) matrix, and confirmed the improvement of thermal stability and stiffness of the polymer through tensile tests [6]. Although existing monitoring methods have certain monitoring capabilities for karst collapse terrain changes, the monitoring data they obtain still cannot provide early warning of collapse time and cannot meet the needs of real-time and intelligent monitoring and analysis of underground deformation.

2. Polylactic Acid Nano TiO_2 Composite Material

2.1 Nano TiO_2 and Polylactic Acid

Nano TiO_2 refers to titanium dioxide materials with nanoscale [7], whose crystal phases include anatase and rutile phases. Due to its wide bandgap nature and excellent characteristics such as low price, high photocatalytic activity, good stability, and environmental friendliness, it has shown broad application prospects in textiles, coatings, medical treatment, and sensing.

However, in practical applications, nano TiO_2 has problems of low light utilization and poor degradation [8]. The photocatalytic degradation mechanism of nano TiO_2 is to adsorb organic matter on the surface of the material and generate active species (such as hydroxyl groups, superoxide radicals, etc.) under ultraviolet light, causing the organic matter to be oxidized, achieving the goal of degrading organic matter. However, due to its poor utilization efficiency under visible light, its degradation efficiency in natural light environments is not high. In addition, due to the significant hydrophilicity and strong electrostatic effect of nano TiO_2, it is difficult to disperse in water and prone to agglomeration. The surface of nano TiO_2 contains a large number of functional groups such as hydroxyl and titanium oxide, which endow it with good hydrophilicity, making it easy to form hydrogen bonds with water molecules and then aggregate in aqueous solutions. Meanwhile, due to electrostatic interactions, particles adsorb and agglomerate with each other, thereby affecting their catalytic performance and degradability.

PLA is a biodegradable biopolymer material. It is based on lactic acid monomers and is mainly produced from plants (such as corn, sugarcane, etc.), with advantages such as environmental protection and renewable energy [9]. PLA has played a great role in medical, packaging and other fields due to its excellent biocompatibility [10]. Using PLA as a carrier to coat the surface of TiO_2 nanoparticles can effectively improve their dispersion and stability, improve their dispersion, reduce particle aggregation, and enhance their photocatalytic performance. In addition, the excellent processing performance and biocompatibility of PLA can improve the degradability of materials. This article combines PLA with nano TiO_2 to solve the problems of low light utilization and poor degradation of nano TiO_2 through composite material preparation methods, in order to achieve sustainable development and application of materials [11].

ISSN 2616-5880 Vol. 4, Issue 7: 83-88, DOI: 10.25236/AJMC.2023.040713

2.2 Material Preparation

2.2.1 Preparation and Modification of Nano Titanium Dioxide

The main materials and equipment for the preparation and modification experiments of nano titanium dioxide are shown in Tables 1 and 2:

Table 1: Main materials for preparation and modification of nano TiO_2

Sequence	Material	Specifications
1	Titanium tetrachloride solution	5 milliliters
2	Glacial acetic acid	45 milliliters
3	Distilled water	180 milliliters
4	Concentrated ammonia water	2 milliliters
5	Acetone	180 grams
6	Tetraethyl orthosilicate (TEOS)	4.5 grams

From Table 1, it can be seen that the main materials used for the preparation and modification of nano TiO_2 include titanium tetrachloride solution, glacial acetic acid, distilled water, concentrated ammonia water, acetone, and TEOS.

Table 2: Main equipment for preparation and modification of nano TiO_2

Sequence	Device	Specifications
1	High pressure reaction kettle	SLP4500
2	Vacuum drying oven	TY669-YB-Z
3	Thermostatic water bath pot	TT30-SYG-A2-6
4	Magnetic stirrer	GL-5250B

In Table 2, the main equipment for preparing and modifying nano TiO_2 includes a high-pressure reactor, a vacuum drying oven, a constant temperature water bath, and a magnetic stirrer.

In the preparation process of nano TiO_2, 5 milliliters of 6.7 moles of titanium tetrachloride solution are first added, and it is placed in ice water for cooling and allowed to stand for 50 minutes. 45 milliliters of glacial acetic acid and 60 milliliters of distilled water are added to a beaker, and stirred and blended to produce a mixed solution. The mixed solution is slowly dropped into the cooled nano TiO_2 and titanium tetrachloride solution, stirring it with a magnetic stirrer for 20 minutes. After stirring, it is placed in a water bath for heating treatment at a temperature of 80 ℃. Then, 2 milliliters of concentrated ammonia water are slowly dropped in, and the pH of the solution is adjusted to 8.0. The solution continues to be stirred for 40 minutes. Then, the solution is left to stand for 24 hours at a constant temperature of 95 ℃, then cooled to room temperature, filtered, and washed with distilled water. After repeating the filtration and washing steps 5 times, the product is placed in a vacuum drying oven for drying treatment, and the temperature is set to 80 ℃. Finally, a sample of nano TiO_2 material is obtained.

In the process of modifying nano TiO_2, the prepared nano TiO_2 sample is first placed in a closed space with a cup of water at a room temperature of 27 ℃ and a relative humidity of 70% for 48 hours until the nano TiO2 sample completely absorbs water. Then, 180 grams of acetone and 4.5 grams of TEOS are weighed and added to a flask for stirring, with a time set at 45 minutes. Among them, TEOS, as a coupling agent, can form a stable solution in acetone, making the nano TiO_2 material sample uniformly dispersed for subsequent processing. After stirring acetone and TEOS, nano TiO_2 samples with the same concentration and stable moisture absorption saturation are added. They are then stirred, heated, and cooled at room temperature for 12 hours. Finally, it is placed in a drying oven for 8 hours to obtain a sample of modified nano TiO_2 powder material.

2.2.2 Preparation of Polylactic Acid and Nano TiO_2 Composite Materials

In the preparation process of PLA and nano TiO_2 composite materials, different mass ratios (0%, 0.5%, 1%, 1.5%, 3%) of PLA are first added to a mixer with a speed of 240 times per minute, and a temperature condition of 160 ℃ is set. Under this condition, the modified nano TiO_2 powder sample is placed in the mixer and mixed with PLA. The stirring time is set to 2 hours. Then, the stirred product is placed on a hot press for hot pressing treatment, and the temperature is set to 180 ℃, followed by 2 minutes of pressurization, followed by 20 seconds of exhaust. This step is repeated three times, and finally cooled to room temperature to obtain samples of PLA and nano TiO_2 composite materials with different mass ratios.

ISSN 2616-5880 Vol. 4, Issue 7: 83-88, DOI: 10.25236/AJMC.2023.040713

3. Performance Characterization and Degradation Behavior

In order to understand the performance of the prepared PLA nano TiO_2 composite material samples, this article conducts performance standards and degradation behavior analysis, and verifies it from two aspects: its crystallization performance and degradability. According to the formula in material preparation, the obtained material samples are sequentially labeled as samples 1 to 5. The material ratio is shown in Table 3:

Table 3: Material ratio

Sequence	PLA mass ratio	Hot pressing treatment time
Sample 1	0%	5 minutes
Sample 2	0.5%	10 minutes
Sample 3	1%	10 minutes
Sample 4	1.5%	10 minutes
Sample 5	3%	10 minutes

In Table 3, except for sample 1 with a PLA mass fraction ratio of 0%, which has a heat treatment time of 5 minutes, all other material samples have a heat treatment time of 10 minutes.

3.1 Crystallization Performance Characterization

Crystal structure is a key factor affecting the photocatalytic activity and dispersibility of materials. Materials with good crystallization performance generally have a larger specific surface area and a uniform crystal structure, which is conducive to the utilization of light energy and charge transfer. To highlight the characterization effect, this article only selects material samples with a PLA mass ratio of 0.5% and a material sample with a mass ratio of 3% for comparison of crystallization performance. The final characterization results are shown in Figure 1:

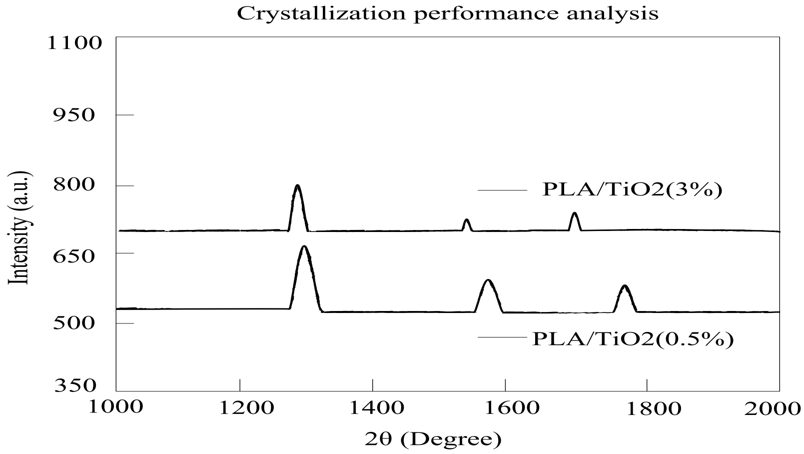

Figure 1: Crystallization performance characterization results

In Figure 1, the horizontal axis is 2, which is expressed in degrees, and the vertical axis is strength, which is expressed in degrees. From Figure 1, it can be seen that there are significant differences in the characterization of material crystallization performance under different PLA mass ratios. Compared with the material sample with a PLA mass ratio of 0.5%, the diffraction peak width of the material sample with a PLA mass ratio of 3% is smaller and its morphology is sharper. This indicates that the material sample with a PLA mass ratio of 3% has better crystallization performance and a more orderly atomic arrangement in its lattice. In practical applications, its structure is more conducive to the transmission of electrons in materials, reducing the probability of electron scattering and recombination, thereby improving the lifespan and mobility of photo generated carriers, and providing more active sites for photocatalytic reactions.

3.2 Degradability

The degradability of materials plays an important role in sustainable development. To analyze the degradability of the prepared composite materials, the material samples are placed in a high

ISSN 2616-5880 Vol. 4, Issue 7: 83-88, DOI: 10.25236/AJMC.2023.040713

temperature and humidity environment for 15 days, and weighed every three days using a balance to record the weight changes of the samples. The greater the weight loss, the better the degradability of the material. It is assumed that the weight of the material sample before the experiment is W_B, and the weight of the material sample after the experiment is W_A. The degradability rate of the material sample is set as D_I, and the calculation formula is:

$$D_I = \frac{W_A - W_B}{W_B} \times 100\% \tag{1}$$

According to formula 2, the degradation rate results of each material sample during the experimental period are shown in Figure 2:

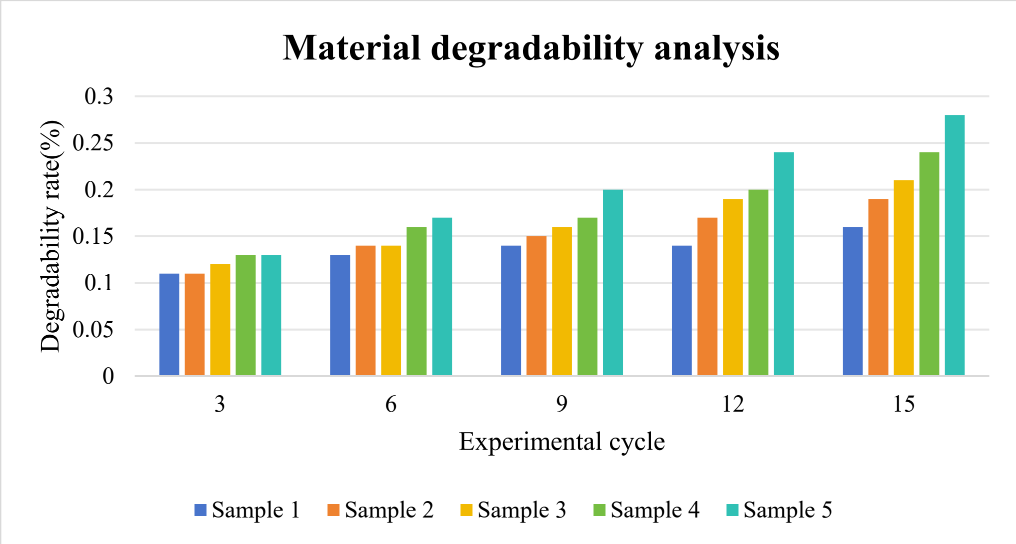

Figure 2: Degradability results

From Figure 2, it can be seen that the degradability of the material sample varies with the increase of the standing time. When left in a high-temperature and high humidity environment for 3 days, the degradability rates of material samples 1 to 5 are 0.11%, 0.11%, 0.12%, 0.13%, and 0.13%, respectively. At this time, the difference in material degradability rates is not significant, mainly due to the short cycle. When left in a high-temperature and high humidity environment for 15 days, the degradability rates of material samples 1 to 5 are 0.16%, 0.19%, 0.21%, 0.24%, and 0.28%, respectively. From the comparison results, the higher the PLA mass ratio, the more significant the material's degradability. Compared with the material with a PLA mass ratio of 0%, the degradation rate of the material sample with a PLA mass ratio of 3% ultimately increases by 0.12%.

4. Conclusions

Nano TiO_2 has excellent photocatalytic performance and is widely used in fields such as healthcare and food packaging. However, there are certain limitations in its degradability, which limits its sustainable development. In order to improve the degradability and application value of the material, this article combined PLA with nano TiO_2 to form a composite material, and studied its preparation, characterization, and degradation behavior. Compared with a single nano TiO_2 material, the composite material composed of PLA and nano TiO_2 had a more excellent crystal structure and greatly improved its degradability. The preparation, characterization, and degradation behavior of PLA nano TiO_2 composite materials in this article have certain guiding significance in improving the sustainable development of materials, but there still are shortcomings. In future research, it would be necessary to continuously improve the research quality from the perspective of material functionality, and promote the high-quality development of composite materials in the field of environmental applications.

Acknowledgement

This work was supported by the youth research project of Taizhou Vocational College of Science & Technology(23QNB08);The visiting engineer school-enterprise cooperation project of Zhejiang Province, China(FG2022384);The science and technology plan project of Taizhou City, Zhejiang

ISSN 2616-5880 Vol. 4, Issue 7: 83-88, DOI: 10.25236/AJMC.2023.040713

Province, China(23gyb26).

References

[1] Chi Hai, Wenhui Li, Chunli Fan, Cheng Zhang. "Effect of High Pressure Treatment on Poly (lactic acid)/Nano–TiO_2 Composite Films." Molecules 23.10 (2018): 2621-2633.
[2] Tajdari Ali, Amir Babaei, Alireza Goudarzi, and Razie Partovi. "Preparation and study on the optical, mechanical, and antibacterial properties of polylactic acid/ZnO/TiO_2 shared nanocomposites." Journal of Plastic Film & Sheeting 36.3 (2020): 285-311.
[3] Zhang Zheng, Yang Wang, Ting Li, Piming Ma, Xuhui Zhang, Bihua Xia, et al. "High-performance polylactic acid materials enabled by TiO_2–polydopamine hybrid nanoparticles." Industrial & Engineering Chemistry Research 60.10 (2021): 3999-4008.
[4] Chenggang Liao, Kang Chen, Ping Li, Xingong Li & Yingfeng Zuo. "Nano-TiO_2 modified wheat straw/polylactic acid composites based on synergistic effect between interfacial bridging and heterogeneous nucleation." Journal of Polymers and the Environment 30.7 (2022): 3021-3030.
[5] Xuebin Hou, Yibing Cai, Mushtaq Muhammad, Xiaofei Song, Qiang Yang, Fenglin Huang, et al. "Deposition of TiO_2 nanoparticles on porous polylactic acid fibrous substrates and its photocatalytic capability." Journal of nanoscience and nanotechnology 18.8 (2018): 5617-5623.
[6] Athanasoulia Ioanna-Georgia, Maria Mikropoulou, Sofia Karapati, Petroula Tarantili, Christos Trapalis. "Study of thermomechanical and antibacterial properties of TiO_2/Poly (lactic acid) nanocomposites." Materials Today: Proceedings 5.14 (2018): 27553-27562.
[7] Li Wei, Kewang Zheng, Hujian Chen, Shirong Feng, Wei Wang and Caiqin Qin. "Influence of nano titanium dioxide and clove oil on chitosan–starch film characteristics." Polymers 11.9 (2019): 1418-1432.
[8] Wenjuan Tan, Jose R. Peralta-Videa, and Jorge L. Gardea-Torresdey. "Interaction of titanium dioxide nanoparticles with soil components and plants: current knowledge and future research needs–a critical review." Environmental Science: Nano 5.2 (2018): 257-278.
[9] Singhvi M. S., Zinjarde S. S., and Gokhale D. V. "Polylactic acid: Synthesis and biomedical applications." Journal of applied microbiology 127.6 (2019): 1612-1626.
[10] Siakeng Ramengmawii, Mohammad Jawaid, Hidayah Ariffin, S. M. Sapuan, Mohammad Asim, Naheed Saba. "Natural fiber reinforced polylactic acid composites: A review." Polymer Composites 40.2 (2019): 446-463.
[11] Hanyur Abdullah. Functional Polymer Materials in Environmental Biosensors in the Context of the Internet of Things. Academic Journal of Environmental Biology (2022), Vol. 3, Issue 3: 60-68.