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# Optimization of the preparation process of biodegradable masterbatches and characterization of their rheological and application properties

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ABSTRACT

Using glycerin as a plasticizer, polylactic acid (PLA) and titanium dioxide ($TiO_2$) were blended and granulated using a twin-screw extruder to obtain a biodegradable white color masterbatch. The rheological properties of the masterbatch were characterized by a torque rheometer and a melt flow rate (MFR) tester. The dyeing force of the sample was characterized by measuring its whiteness index, lightness index, and yellowness index using a color meter, while the opacifying ability of the sample was characterized by measuring its light transmittance with a haze meter. Temperature sensors were set up in each zone of the extruder screws to measure their temperatures in real time. By using quadratic orthogonal rotation combination design, and in conjunction with a response surface methodology (RSM), the effects of processing conditions, such as screw shear speed, processing temperature, and glycerin content, on the opacifying ability of white PLA masterbatch were studied. In addition, Design-Expert software was used to simulate the relationship between various processing conditions and the opacifying ability of white PLA masterbatch. The experimental results showed that, when the glycerin content was 1%, the whiteness index of the masterbatch was highest and its color was brightest. When the glycerin content was 3.22%, the light transmittance of the masterbatch was lowest and its opacifying ability was strongest. This paper was the first to use response surface methodology to study optimization of the preparation process for biodegradable masterbatches.

## 1. Introduction

Due to the intensification of white pollution and the shortage of global petroleum resources, biodegradable plastics, such as polylactic acid (PLA), poly (butyleneadipate-co-terephthalate) (PBAT), are increasingly used in packaging, daily necessities, and medical applications [1,2]. In the processing of these products, color masterbatches are often used for coloration. However, the vast majority of color masterbatches in today's market are prepared using conventional polymers, such as LLDPE and LDPE [3], as carriers. Because color masterbatches based on these traditional polymers are not biodegradable, products made from these masterbatches are also not biodegradable. Therefore, in order to ensure the biodegradability of final products, color masterbatches and the carriers used in them must be biodegradable. The carrier polymer of biodegradable color masterbatches can be PLA, polyhydroxyalkanoates (PHA), and polybutylene succinate (PBS). Among these biodegradable materials, PLA has become a hotspot of development and research in recent years [4]. The filler of biodegradable masterbatches can be talc, silica, calcium carbonate, starch or cellulose [5], and the dispersant can be glycerin, corn oil or cleanse oil [6].

White color masterbatches are often used to color injection-molded products such as knives, forks, and spoons. The white color of these products is mostly produced by the solid pigment titanium dioxide ($TiO_2$). $TiO_2$ is a nontoxic, light, high gloss material with a high refractive index and a high scattering rate [7,8]. Due to its high refractive index and excellent opacifying ability, $TiO_2$ is superior to other white pigments and is widely used in white color masterbatches. Opacifying ability or opacity is an important indicator of the dyeing performance of white color masterbatches because it represents the performance of the pigment in terms of light absorption, scattering and reflection. Opacity also reflects the ability of the coating to cover the surface color of the substrate [9]. With an identical pigment addition, the pigment with better opacifying ability will produce lighter and thinner plastic products with the same level of whiteness. When the mass fraction of $TiO_2$ in the carrier is higher than 30%, the viscosity of the polymer system

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rapidly increases, which reduces the processability of the material [10] and requires the use of a plasticizer to adjust the viscosity of the system. Sarazin et al. [11] used glycerin as a plasticizer for PLA/TPS composites and found that the effect of plasticization was significant. Because of the significant impact of the process parameters on the properties of the composite [12], the type of plasticizer, toner content, screw shear rate, and processing temperature all influence color masterbatch processing and coloring performance. Therefore, in order to optimize the effects of various processing conditions on the use performance of biodegradable masterbatches, it is particularly important to find a method that can optimize their preparation process.

Using polylactic acid as the carrier for color masterbatches, $TiO_2$ as the pigment toner and glycerin as the plasticizer, an optimized method for the preparation of biodegradable masterbatches with high opacifying ability was developed. The biodegradable resin, plasticizer, and pigment were placed into a twin-screw extruder for granulation. In addition, temperature sensors were set up in each zone of the extruder screws to automatically collect temperatures and other process parameters during processing. Furthermore, response surface methodology (RSM) was used in conjunction with a three-variable quadratic regression equation and orthogonal rotation experiments to analyze the preparation processes and study the factors affecting the opacifying ability of the biodegradable masterbatch during extrusion granulation.

RSM is an optimization method combining experimental design with statistics [13]. It includes numerous methods, such as experimental design, modeling, testing, model suitability, and searching for the best combination of conditions. Through regression fitting and response surface analysis, the response value at the level of each factor can be easily calculated [14]. RSM is widely used in the preparation of composite materials and optimization of process variables [15–17], but its use in masterbatch preparation has not been reported.

## 2. Experimental

### 2.1. Materials

PLA (4032D, NatureWorks, USA): vitrification temperature of 55–60 °C, melt index of 7 g/10 min, and peak melting temperature of 155–170 °C;

$TiO_2$ (Shanghai Sinopharm Group): relative density of approximately 4.0;

Glycerin (AR, Shanghai Sinopharm Group): boiling point 290 °C.

### 2.2. Principal equipment used

Twin-screw extrusion granulator, DT-20, Screw diameter: 20 mm, L/D: 44, Nanjing Dingtian Machinery Manufacturing Co., Ltd.

Twin-screw film blower, XSS-300, Shanghai Kechuang Rubber and Plastic Machinery Equipment Co., Ltd.

Torque rheometer, XSS-300, Shanghai Kechuang Rubber and Plastic Machinery Equipment Co., Ltd.

Electric thermostatic blast drying oven, DHG-9245A, Shanghai Yiheng Technology Co., Ltd.;

High speed mixer, SHR-10A, Suzhou Shengguang Plastic Machinery Co., Ltd.;

Melt flow rate (MFR) tester, XNR-400, Jinjian Detection Instrument Co., Ltd.;

Digital haze meter, NDH-20D, Feng Cheng Power Equipment Co., Ltd.;

Automatic color meter, SC-80C, Beijing Kangguang Instrument Co., Ltd.

### 2.3. Sample preparation

#### 2.3.1. Masterbatch preparation

The masterbatch used for testing consisted of three parts: colorant, carrier, and plasticizer. The carrier was PLA, the colorant was titanium dioxide, and the plasticizer was glycerin. The specific formulations are listed in Table 1.

**Table 1**
Process formulations of the masterbatches.

| PLA (Wt%) | GI (Wt%) | TiO2 (Wt%) |
|---|---|---|
| 70 | 0 | 30 |
| 70 | 1 | 30 |
| 70 | 3 | 30 |
| 70 | 5 | 30 |
| 70 | 7 | 30 |

PLA and $TiO_2$ were placed into a high-speed mixer and mixed at 100 °C for 20 min, followed by the addition of glycerin. After even mixing, the mixture was placed into a twin-screw extruder to produce granules. For the twin screws, the temperature from the inlet to the screw head was 120–155 °C, and the screw movement frequency was 30 Hz.

#### 2.3.2. Preparation of thin films

PLA resin was premixed with the masterbatch described in section 2.3.1 (the content of $TiO_2$ in the pigmented resin was 1%) and put into the extruder/film blower. The temperatures for the three stages of film blowing were 165 °C, 175 °C, and 180 °C.

#### 2.3.3. Preparation of sample plates

PLA resin was premixed with the masterbatch described in section 2.3.1 (the content of $TiO_2$ in the pigmented resin was 1%) and put into the torque rheometer. After further mixing, the mixture was pressed into plates. The temperature of the torque rheometer was set to 170 °C, 175 °C, or 180 °C. The rotation speed was 60 rpm, and the processing time was 8 min. The press temperature was 190 °C.

#### 2.3.4. Design of RSM based on opacifying ability

(1) Design of experiments based on a CCD [18,19] model.

The experimental design was based on a two-level factorial design plus the extreme points and the center point. Usually, the experimental table was coded and then converted into actual operating values. In general, the values were 0, ± 1, and ± α, where ± 1 were the cubic points and were also called the corner points. There were a total of $2^k$ corner points. The value of 0 was the center point, and α was the axial point, whose value was given by the formula $\alpha = F^{(1/4)}$, where F was the number of experiments for the factorial design. $F = 2^k$, and k was the number of factors.

In this experiment, a combination design of ternary quadratic regression and orthogonal rotation was used to obtain the following values: k = 3, F = 8, and α = 1.68. Based on these values, a group of 20 experiments was designed, of which the number of factorial experiments was 8 and the number of star points was 6, while 6 center point repetitions were performed to ensure uniform precision.

Three factors, i.e., glycerin content (A), twin-screw frequency (B), and maximum temperature of twin screw processing (C), were selected as independent variables, and 5 levels were assigned for each factor and coded as 0, ± 1, and ± 1.68, respectively. The light transmittance of the masterbatch was used as the response value to design a 3-factor, 5-level test. The specific experimental factors and level design are shown in Table 2.

(2) According to the experimental conditions specified in Table 3, the masterbatch was prepared by twin-screw extrusion and granulation.
(3) Using the masterbatch prepared in Table 3, films and sample plates were prepared according to 1.3.2 and 1.3.3.