Material behaviour

# Comparison of the effects of commercial nucleation agents on the crystallization and melting behaviour of polylactide

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## ARTICLE INFO

## ABSTRACT

The effects of eight commercial nucleation agents on the crystallization of polylactide (PLA) were comparatively investigated by differential scanning calorimetry. Among them, TMC-328 (TMC) and PET-C (PETC) show significant nucleation effects on PLA. Under the same nucleation agent content, the crystallization temperatures of PLA/TMC samples are about 15 °C higher than those of PLA/PETC samples at the same cooling rate. However, PETC accelerates the crystal growth of PLA more effectively than TMC. Due to the high crystallization temperatures, the crystals nucleated by TMC are more perfect than those nucleated by PETC. The PLA/PETC samples show double melting peaks. The PLA/TMC samples are more transparent than the PLA/PETC samples. However, TMC promotes the degradation of PLA more seriously than does PETC.

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## 1. Introduction

Polylactide (PLA) is highly important today as a biodegradable and bio-based plastic. It has been widely applied, including in medical apparatus, textiles, packaging and cutlery. However, several disadvantages limit its commercialization, such as its stiffness and brittleness [1–4], poor thermal stability [5,6], and relatively low crystallization rate [7,8]. Thus, modification of PLA is necessary to broaden its application.

PLA can be semicrystalline or amorphous depending on the stereochemistry [7]. For crystallizable PLA, its crystallization rate is quite low, and no obvious crystallization proceeds under practical molding conditions because of the high cooling rate. Only almost totally amorphous articles can be obtained, which results in a low heat deflection temperature and unstable mechanical properties. Nucleation agents (NAs) are widely used for semicrystalline polymers to accelerate the crystallization rate. Some chemicals have been examined to serve as NAs in PLA. Talc

is a simple and readily available NA for PLA crystallization [9,10]. However, the nucleation effect is not good enough, and the addition of talc reduces the physical properties of PLA [10]. Some organically modified montmorillonite clay [11,12], aliphatic amides [13,14], and hydrazide compounds [15] have also been found to have the ability to nucleate the crystallization of PLA. Although research has been done, the industrial production of NAs for PLA has barely started. NJStar TF-1, an amide compound developed by New Japan Chemical Co., Japan, is a commercial PLA NA that can reduce the PLA production cycle time by 17% with improved heat and shock resistance. In 2009, a new NA for PLA was announced by Shanxi Provincial Institute of Chemical Industry, China (SPICI), named TMC-328.

There are a number of commercial NAs for polypropylene, poly(ethylene terephthalate) and other semicrystalline plastics. A fast and effective way to develop new NAs for PLA is by using commercial NAs. However, there is a dearth of published literature [10] that examines this approach. In this paper, we investigate eight commercial NAs listed in Table 1 (one designed for PLA and seven designed for other polymers) to determine whether they can effectively enhance the crystallization of PLA. The non-isothermal crystallization kinetics, the melt behaviour, the

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**Table 1**
Nucleation agents used in this study.

| Code | Name | Component | General use |
|------|------|-----------|-------------|
| M3988 | Millad 3988 | sorbitol derivative | PP |
| HPN68L | Hyperform HPN-68L | carboxylic acid sodium salt | PP |
| WBGII | WBG-II | rare-earth organometallic derivative | PP |
| TMB | TMB-5 | amide compound | PP |
| P22 | Bruggolen P22 | mixture of organic and inorganic nucleation agents | PA |
| P250 | Bruggolen P250 | mixture of organic and inorganic nucleation agents | PET, PP |
| PETC | PET-C | organically modified montmorillonite clay | PET |
| TMC | TMC-328 | amide compound | PLA |

transparency and thermal stability of PLA in the presence of the two most effective NAs are studied in detail.

## 2. Experimental

### 2.1. Materials

The PLA pellets with grade name 4032D and comprising around 2% D-lactide were supplied by Natureworks LLC, USA. Commercial NAs used in this study were Millad 3988 and Hyperform HPN-68L (Milliken Co. USA), Bruggolen P22 and P250 (Brüggemann Chemical Co. USA), WBG-II (Guangdong WINNER Functional Materials Co. China), PET-C (Beiqing Nano P&R Co. China), TMB-5 and TMC-328 (SPICI, China). The components and their general uses are listed in Table 1. Dichloromethane and chloroform were purchased from Sinopharm Chemical Reagent Co., China.

### 2.2. Sample preparation

The PLA pellets and NAs were dried at 80 °C under vacuum for 6 h and then blended in an internal mixer (KCCK, China) at 180 °C and 100 r/min for 6 min. The NA contents studied were 0.2, 0.5, and 1.0% by weight. Neat PLA was also processed in the same way to obtain a reference material. The sample containing 0.5% TMC, similar to the other samples, is denoted as PTMC-0.5 in subsequent discussions. Before measurements were made, the samples were again dried at 80 °C under vacuum for 6 h.

### 2.3. Measurements

A TA differential scanning calorimeter (DSC) 2910 (TA, USA) was used for calorimetric investigations. About 8 mg of each sample was placed in an aluminum pan and heated from room temperature to 200 °C, with 3 min holding to eliminate the thermal history. They were then cooled to 5 °C at a set cooling rate. The cooling rates employed in this study were 2.5, 5, and 10 °C/min. After 3 min holding at 5 °C, the samples were reheated to 200 °C at 10 °C/min to record their melting behaviour. All DSC measurements were carried out under a nitrogen atmosphere at a flow rate of 50 ml/min.

The samples for wide-angle X-ray diffraction (WAXD) and visible light transmission measurements were firstly non-isothermally crystallized at a cooling rate of 10 °C/min from 200 °C to room temperature using a Mettler FP82 hot stage with a Mettler FP90 central processor (Mettler, Switzerland).

WAXD measurements were performed using a Rigaku D/max 2550 VB/PC X-ray diffractometer (Rigaku, Japan) with a CuKa source at room temperature. The voltage and current were set to be 40 kV and 100 mA, respectively. Step size of the scan was chosen to be 0.02.

The transparency of the samples was measured by an ultraviolet-visible-near infrared spectrophotometer (Cary 500, Varian, USA). The wavelength range was from 400 nm to 800 nm.

In order to measure the intrinsic viscosity ($IV$) of PLA, each sample was dissolved in dichloromethane and then filtered to remove any impurities. Afterwards, the solvent was allowed to volatilize at room temperature for two days, leaving a thin layer of PLA residue. After drying at 50 °C under vacuum for another two days, the purified sample were then dissolved in chloroform at approximately 1 g/dL concentration. The $IV$ value was measured using a Ubbelohde viscometer at 30 °C, according to the Solomon-Ciută equation [16].

## 3. Results and discussion

### 3.1. Comparison of commercial nucleation agents

The effects of the commercial NAs used in this study were evaluated using DSC. Fig. 1 shows the DSC cooling curves of neat PLA and PLA/NA at the same cooling rate of 10 °C/min. The NA content was 0.5% by weight.

The peak crystallization temperature ($T_c$), crystallization enthalpy ($\Delta H_c$) and degree of crystallinity ($X_c$) are shown in Table 2. $X_c$ was calculated from:

$$X_c = \frac{\Delta H_c}{\Delta H_m^0} \times 100\% \tag{1}$$

where $\Delta H_m^0$ is the melt enthalpy of fully crystalline PLA, which was taken as 93 J/g [17].
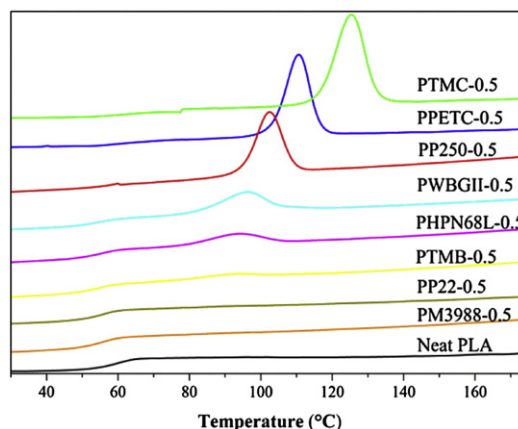


**Fig. 1.** DSC cooling curves for neat PLA and PLA/NA at 10 °C/min.