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Investigating the crystallization behavior of poly(lactic acid) using CdSe/ZnS quantum dots as heterogeneous nucleating agents

Xinghou Gong [a, b], Ling Pan [a], Chak Yin Tang [b, *], Ling Chen [b], Chunqing Li [a], Chonggang Wu [a], Wing-Cheung Law [b], Xiaotao Wang [a], Chi Pong Tsui [b], Xiaolin Xie [c]

[a] *Hubei Provincial Key Laboratory of Green Materials for Light Industry, Collaborative Innovation Center for Green Light-weight Materials and Processing, School of Materials Science and Engineering, Hubei University of Technology, Wuhan, Hubei Province 430068, PR China*

[b] *Department of Industrial and Systems Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, PR China*

[c] *Key Laboratory for Large-Format Battery Materials and System of National Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, Hubei Province 430074, PR China*

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ABSTRACT

Heterogeneous nucleation is a frequently encountered phenomenon in the crystallization of inorganic nanoparticle/polymer systems, and has a great influence on the morphology and properties (such as optical, mechanical and degradable properties) of the nanocomposites. In this study, a solution casting method was adopted to fabricate CdSe–ZnS quantum dots (QDs)/poly(lactic acid) (PLA) nanocomposites films of various QDs concentrations by using chloroform as the solvent. Fourier transform infrared (FT-IR) spectroscopy, polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffractometry (XRD) were used to characterize the crystallization behavior of the nanocomposites films that had been thermally treated differently from the as-cast state. The FT-IR and POM results showed that the nucleation density and the crystallization ability of PLA are greatly enhanced with addition of the QDs in the processes of isothermal crystallization at 403 K. The results of DSC revealed that the glass transition temperature of PLA has no obvious change with the addition of QDs. For the QDs/PLA samples which were isothermally annealed at 403 K for 30 min, the degree of (melt) crystallinity increased with increase of QD concentrations in the PLA matrix. All the results obtained from FT-IR spectroscopy, POM, DSC, and XRD were consistent, suggesting that the CdSe–ZnS QDs can serve as an efficient heterogeneous nucleating agent for the acceleration and enhancement of the melt crystallization of PLA at the optimized condition.

1. Introduction

The polymer crystallization process has been of great interest for many decades. One of the important reasons is that the physical or mechanical properties can be improved after the crystallization, thus conferring the feasibility for a wide range of applications [1–4]. For example, poly(lactic acid) (PLA), a biocompatible and bioresorbable semicrystalline polyester that can be derived from renewable resources, has been extensively used in the plastics and medical industries, and is being recognized as a potential replacement for petroleum-based plastics [5,6]. Amorphous PLA possesses poor heat resistance because of the weak mechanical strength when the temperature is above its glass transition temperature (T_g), which is ~333 K [7]. After fully crystallizing the PLA, the Vicat penetration temperature and heat deflection temperature were increased by 100 K and 30 K respectively and the flexural modulus, impact resistance and strength were increased remarkably. With enhanced strength, the enzymatic degradation rate can be reduced by more than 7 fold. Furthermore, oxygen and water vapor permeability coefficients were decreased by more than 4 fold and 3 fold respectively. In fact, the polymer crystallinity has played an important role in determining the physical properties which can be employed for different applications.

The effects of PLA crystallinity on its properties, crystal structure and crystallization behavior of PLA have been widely studied using many techniques over the years. Under different specific conditions, α, β and γ crystalline forms (modifications) of PLA can be prepared [8,9]. For instance, the most common modification, α-

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* Corresponding author. Tel.: +86 85227666608; fax: +86 85223625267.
E-mail address: mfcytang@polyu.edu.hk (C.Y. Tang).

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form with a left-handed 10_3 helical chain conformation was grown in the process of normal melt, cold, low-drawing-ratio or solution crystallization. The β modification, with a left-handed 3_1 helical chain conformation, can be obtained from high hot-drawing ratios, mechanical stretching of the more stable α-form or solution-spinning processes conducted at high temperatures [10]. The γ form was developed from the epitaxial crystallization [11]. In recent years, a new limited-disordered 10_3 helical chain conformation, named α′-form, has been reported by Pan et al. [12]. They suggested that the PLA showed α-form characteristics when the crystallization temperature was above 393 K, while those of the α′-form were found at below 393 K.

However, most PLAs are in an amorphous state and are very difficult to crystallize using common processing methods. The crystallization rate depends on the nucleation rate and the growth rate of the PLA crystals. The number of primary nucleation sites can be improved by the addition of nucleating agents. Research group showed that the TiO_2 incorporation in the PLA matrix can drastically alter the crystallization behavior of PLA [13]. They stereocomplex crystallites formed between PLA and TiO_2 could serve as the nucleating agents. Apart from TiO_2, many researchers have focused on studying the effects of fillers on PLA crystallization, such as SiO_2 [14], organically modified montmorillonite [15], graphene oxides [16], hydroxyapatite [17], carbonated hydroxyapatite [18] and carbon nanotubes (CNTs) [7,19]. Song et al. [20] used the melt blending method to produce nanoscale zinc citrate/PLA composites. A faster overall crystallization rate and a shorter PLA crystallization time were found after the addition of zinc citrate. Zhou et al. [18] reported on a carbonated hydroxyapatite/PLLA composite prepared by a selective laser sintering technology. The results showed that the carbonated hydroxyapatite is an efficient nucleating agent for PLA. At the same time, they also mentioned that the crystallization process assisted by the fillers was also influenced by the thermal history (i.e. the operating temperatures and cooling rates) [18]. A commonly used inorganic filler, CNT, was used as an effective nucleating agent by Liang et al. in a PLA matrix [19]. The results indicated that the crystallization of PLA was governed by the surface modification, the dispersion state and the concentration of CNTs.

Semiconductor nanocrystals, or so-called quantum dots (QDs), have attracted a great deal of attention in recent years due to their unique optical and electronic properties [21,22]. In our previous study, the use of CdSe–ZnS QDs as a fluorescent label was mixed with PLA to fabricate CdSe–ZnS/PLA scaffolds [23] and films [24], by solvent casting/vacuum volatilization/particulate leaching (SC/VV/PL) method and solvent casting method, respectively. QDs have found wide potential applications in the field of optoelectronics. However, little is known about the effects of luminescence QD, as a nucleating agent in QD/PLA nanocomposites. In this study, CdSe–ZnS QDs/PLA nanocomposite films, with QD/PLA ratios varying from 0.25 to 2.0 wt%, were prepared by a solution casting method. A combination of characterizations, Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), X-ray diffractometry (XRD) and polarized optical microscopy (POM), were used to investigate the effect of the CdSe–ZnS QDs on the crystallization behavior of PLA matrix.

2. Materials and experiments

2.1. Materials

Poly(lactic acid) (PLA) pellets were purchased from Shenzhen-City Bright China Industrial Co., Ltd., China, with a number average molecular weight of about 84,000 determined by size exclusion chromatography (SEC) (Agilent, 1100 HPLC). Core-shell CdSe–ZnS QDs coated with tri-*n*-octylphosphine oxide (TOPO) were obtained from Wuhan-City Jiayuan Quantum Dots Co., Ltd., China, where the QDs were dissolved in chloroform with a mass concentration of 3.5 mg/ml, as detected by thermogravimetric analysis (TGA), and the quantum yield of the QDs estimated by comparison to the PL intensity of Rhodamine 101was 74%. Chloroform was purchased from Tianjin-City Fuchen Chemical Reagent Factory, China. All of the reagents were of analytical grade and used without further treatment.

2.2. Preparation of CdSe–ZnS QDs/PLA nanocomposites

0.5 g of PLA was dissolved in chloroform to obtain a 5 wt% solution. A predetermined volume of the CdSe–ZnS QDs solution in chloroform was added into the PLA solution under stirring. The resulting CdSe–ZnS/chloroform/PLA mixture was sonicated for 10 min in an ultrasonic bath to ensure uniform dispersion of the CdSe–ZnS, which was then cast on a Petri dish: six CdSe–ZnS/PLA films with thicknesses of ca. 0.1 mm were obtained upon air drying of the mixtures for 24 h followed by vacuum drying (<1 mmHg) for another 48 h at room temperature. According to the different weight percentages (0, 0.25, 0.5, 1, 1.5 and 2 wt%) of the CdSe–ZnS QDs in the PLA, the six films were labeled PLA, 025QDs/PLA, 05QDs/PLA, 1QDs/PLA, 15QDs/PLA, and 2QDs/PLA, respectively.

2.3. Characterization

A small piece of each of the above six CdSe–ZnS/PLA films was re-dissolved in a small amount of chloroform; the resulting solution was dropped onto a KBr disk, which was then well dried into a thin film on the KBr disk according to the procedure described in Section 2.2. The film was heated to 473 K and held there for 3 min to minimize the effect(s), if any, of its preparation history, which was then quickly cooled (quenched) to a predetermined crystallization temperature (393, 403 or 413 K, respectively). It was subsequently annealed there for 10 min, and finally quenched further to room temperature to prepare the *isothermally-crystallized* sample for FT-IR spectroscopic measurement. For comparison, a fourth (i.e., *melt-quenched*) FT-IR film-sample for each CdSe–ZnS/PLA was prepared in a generally similarly manner but without an isothermal annealing across the quenching process from 473 K to room temperature. The four FT-IR spectra for each composition of CdSe–ZnS/PLA nanocomposite were recorded using an FT-IR spectrophotometer (Thermo Fisher, Nicolet 6700) from 4000 to 400 cm^{-1} IR region.

0.03 g of each composition of the CdSe–ZnS/PLA films was re-dissolved in 3 ml of chloroform, and the formed solution was dropped onto a carbon-film-coated 200-mesh copper grid followed by thorough drying with an infrared lamp for transmission electron microscopy (TEM) (JEOL, 2010HT) observation.

Isothermal spherulitic growth for the PLA in the CdSe–ZnS/PLA nanocomposites was observed on a polarized optical microscope (Leica, DM2500P) equipped with a heating-cooling stage attached to a temperature controller (T95-P1). Film samples on glass slides for the CdSe–ZnS/PLA nanocomposites were prepared using a procedure similar to that for FT-IR spectroscopy. They were then heated to 473 K and maintained for 3 min to minimize any effect(s) of their preparation history, followed by quenching to a predetermined crystallization temperature prior to POM observation of the spherulitic growth.

DSC was carried out on a differential scanning calorimeter (Mettler Toledo, STARe System DSC1) in the temperature range from 298 to 473 K under a nitrogen atmosphere at a heating rate of 10 K/min. Well-dried flake samples of weight 5–10 mg, cut from larger as-cast CdSe–ZnS QDs/PLA films, were encapsulated into