



# Real-time tracking of the hierarchical structure of biodegradable poly(butylene succinate-co-terephthalate) nanocomposites with fibrous attapulgite nanoparticles



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## ABSTRACT

Clearly understanding the structural development of materials during their preparation and processing allows for the fabrication of materials with expected properties that can be tailored for specific applications. In this work, we first presented the generation of poly(butylene succinate-co-terephthalate) (PBST) nanocomposites by combining the polymerization of copolymer with the simultaneous incorporation of fibrous attapulgite (ATP) nanoparticles with good dispersion. The lamellar structure, crystallization behavior and mechanical properties of PBST nanocomposites can be regulated by tuning the content of nanoparticles. The effects of nanoparticle morphology on the structure and properties of PBST nanocomposites with fibrous ATP and spherical silica nanoparticles also were investigated. The question why ATP nanoparticles always bring about faster crystallization rate and larger elongation at break than those caused by silica nanoparticles was answered as well. Furthermore, a schematic for the evolution of the hierarchical structure of PBST nanocomposites at each level during cooling was proposed. It was found that the formation and development of the hierarchical structure of PBST nanocomposites were highly temperature-dependent, and their cumulative growth leads to the final crystalline and hierarchical state. Studies of nanoparticles themselves and detailed changes of polymer structure in various scales are opening pathways for engineering flexible composites that can exploit the advantages of both polymers and nanoparticles.

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## 1. Introduction

Mixing of nanoparticles (NPs) into materials and then fabricating nanocomposites have been practised for decades, for these NPs endowing pristine materials with performance enhancements and further additional opportunities for diverse application fields [1–4]. Particularly, polymeric nanocomposites, incorporating nanoscaled fillers into polymers, have been an area of intense industrial and academic research for their fascinating characteristics such as cost-effective processability, light weight, and controllable improvements of the properties like mechanical, thermal, electrical, optical and magnetic, etc [5–8]. Besides enhancing the associated properties of resultant materials, for

crystalline polymers, NPs also have the ability to alter the nucleation ways and crystallization behaviors no matter the polymers are crystallized in an isothermal or non-isothermal process [9–11].

The microstructure of crystalline polymers normally is hierarchical if viewed on scale from the molecular chains of a few nanometers in width to lamellae of dozens of nanometers in thickness and spherulites of several micrometers in diameter [12,13]. A number of researches have been focused on the investigation of material structure but just limited to one certain scale using various techniques such as X-ray diffraction, scattering and transmission electron microscopy, etc [14–17]. As a matter of fact, however, the final structure and properties of these crystalline materials are determined by the respective development of the structural hierarchy at each level and the interactions between them. Hence, revealing the hierarchical evolution during structural formation is essential in both fundamental researches and practical applications.

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Poly(butylene succinate-co-terephthalate) (PBST), one type of aliphatic-aromatic copolymers, has been intensively investigated on its preparation, molecular structure, biodegradability, thermal and mechanical properties for applications in fibers or yarns [18–21], as well as on the structural evolution of pure PBST and PBST nanocomposites with silica NPs during uniaxial stretching [22–24]. It was reported that introducing silica NPs was beneficial to enhance the mechanical strength and accelerate the crystallization rate of pristine PBST [24]. However, PBST nanocomposites filled by NPs with fibrous morphology and whether the morphology of nanofillers matters to their structures and properties are never referred to. Attapulgite (ATP) is a crystalline hydrated magnesium aluminum silicate clay exhibiting rod morphology with a diameter less than 100 nm and a length between hundreds of nanometers and several micrometers [25,26]. It has large specific surface area, strong adsorptive capacity and high mechanical strength, rendering ATP an excellent candidate for polymeric nanocomposites [27–32]. Furthermore, the development of the hierarchical structures of PBST/ATP nanocomposites at each level, and the interaction between each other have not been revealed, which is supposed to have decisive role in their final structure and properties.

In this contribution, PBST nanocomposites filled with fibrous ATP NPs were fabricated by means of *in situ* polymerization. The effects of NPs content on the distribution, structure and crystallization behavior of pristine PBST copolymer were initially investigated. Then the differences of structure and properties of PBST nanocomposites with fibrous ATP and spheric silica NPs were emphasized to elucidate the influences of NPs morphology. Moreover, the hierarchically structural developments of PBST/ATP nanocomposites during cooling were explored via synchrotron radiation X-ray techniques and microscope observation.

## 2. Experimental

### 2.1. Materials

1,4-butanediol (BD), terephthalic acid (TA), succinic acid (SA) were commercially supplied by Shanghai Linfeng Chemical Reagent Co. Ltd. Titanium tetraisopropoxide (TTiPO) and ATP were supplied by Aladdin Chemical Regents Co., Ltd., China. ATP NPs have an

average diameter of 30 nm and length of 550 nm (see Fig. 1a). All chemicals were of analytical grade and used as received without further purification.

### 2.2. Sample preparation

The pure PBST copolymer was synthesized according to our previous work [19] and the 70 mol% butylene terephthalate unit was selected by adjusting the feeding ratio of SA to TA due to its balance between desirable biodegradability and good mechanical properties. PBST nanocomposites with different contents of ATP NPs were prepared via *in situ* polymerization. Typically, ATP NPs with appropriate contents were dispersed in 22 g of BD with ultrasonic shaking for 1 h and then mixed with 11.7 g of TA, 3.6 g of SA, and 0.2 g of TTiPO as catalyst in a four-necked flask. The specific reaction conditions and procedures were shown in Fig. 1b. The as-prepared products were hot-pressed into films for various measurements. For brevity, PBST with 0, 0.5, 1, 2, and 4 wt% ATP NPs are abbreviated as PBST/ATP-0%, -0.5%, -1%, -2% and -4%, respectively.

### 2.3. Characterizations

The morphologies of PBST/ATP nanocomposites were examined by scanning electron microscopy (SEM) on the JSM-5600LV (Japan) at an accelerating voltage of 10 kV. The fracture surfaces of nanocomposites were all coated with gold prior to examination. Chemical composition was examined by energy dispersive spectroscopy (EDS, IE 3000, U.K.).

Thermal properties of PBST nanocomposites were analyzed via a differential scanning calorimeter (Pyris-1 DSC, Perkin-Elmer). Around 7 mg of sample sealed in an aluminum pan was heated to 210 °C at a rate of 20 °C min<sup>-1</sup> and kept for 3 min before cooling at a rate of 10 °C min<sup>-1</sup> to 30 °C under N<sub>2</sub> atmosphere. Subsequently, the sample was reheated up to 210 °C at 20 °C min<sup>-1</sup>.

Wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS) measurements were performed at the beamline BL16B1 of Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China). The wavelength of X-ray was 0.124 nm. The samples were cooled from 210 to 30 °C at a rate of 10 °C min<sup>-1</sup> on a hot stage (LinKam THSMG600), and simultaneous 2D SAXS or WAXD patterns were recorded. The sample-to-detector distances were

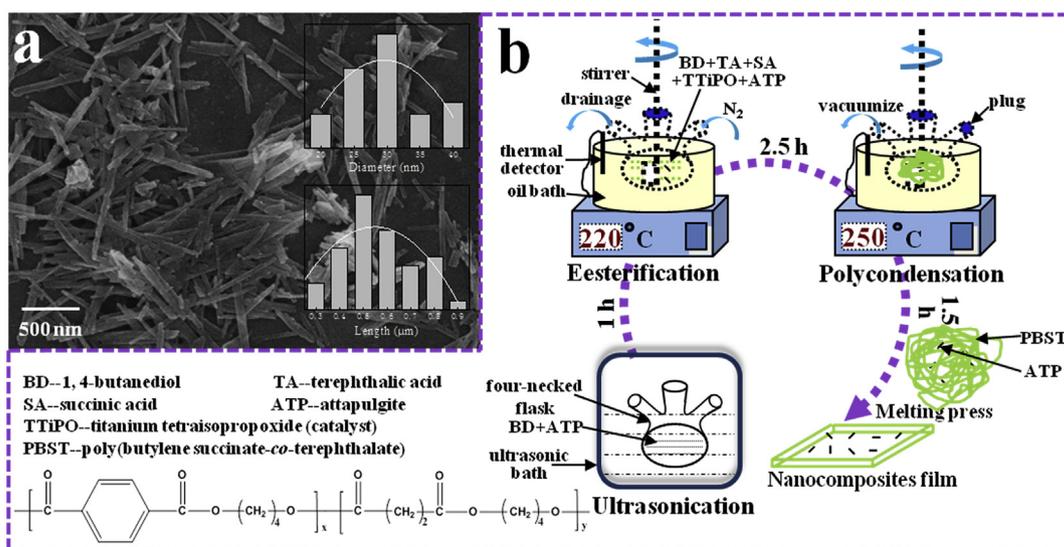


Fig. 1. (a) FE-SEM image of ATP NPs. (b) Schematic illustration of the *in situ* fabrication of PBST nanocomposites with ATP NPs.

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