



# Templated synthesis of nano-sized silica in confined amorphous space of polypropylene



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## ABSTRACT

A template method is a powerful technique to tailor the morphology of formed nanomaterials. The present paper for the first time demonstrated the sol-gel reaction templated by the higher-order structure of semi-crystalline polymer. Silicon alkoxide was impregnated into the amorphous space of polypropylene (PP) with the aid of supercritical CO<sub>2</sub>, and subsequently converted into uniformly dispersed silica nanoparticles. The size and anisotropy of silica nanoparticles were controlled through the amorphous thickness of PP that was preliminarily defined through the crystallization process. We also studied the impact of the silica morphology on physical properties of resultant PP/silica nanocomposites. The silica morphology was systematically varied, keeping relatively uniform dispersion. We revealed that the storage modulus of the nanocomposites was well correlated with the size and anisotropy of the nanoparticles.

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## 1. Introduction

Nano-sized or nano-structured inorganic oxides are indispensable materials applied to a wide variety of fields such as support materials for heterogeneous catalysis [1,2], reinforcing/functionalizing fillers for polymers [3,4], electrode materials in lithium ion batteries, semiconductors for field-effect transistors, and so on [5–9]. An exquisite control of the morphology is achieved by selecting a suitable preparation method from a library of established protocols, depending on desired applications. The sol-gel reaction is a facile and versatile method to synthesize oxides without a need of any special equipment. The morphology of formed oxide nanoparticles or nanostructures are typically controlled through reaction parameters such as pH, temperature, and precursor/solvent ratio [10–19]. A more explicit control is introduced when the reaction is performed using a template of a desired geometry. For example, inorganic oxides with mesoporous channels or hollow tube structures are fabricated by the sol-gel method using self-assembled structure directing agents as a template [20–28]. Nano-wire structures have been obtained for a variety of oxides based on the sol-gel reaction inside a cylindrical template like mesoporous alumina [28–32]. The formed high

aspect ratio morphology has great advantages for electronic device applications including semiconductors and lithium ion batteries, and it can be easily tuned by the template structure [5,8,9]. Hollow oxide nanoparticles can be prepared by sol-gel-derived coating of polymer nanospheres and subsequent removal of the polymer template via incineration or solvent etching [32,33]. Nowadays, the sol-gel template synthesis offers a facile access to a wide variety of morphologies for various oxides, and a material scientist can choose an appropriate combination of templates and oxides from the toolbox according to desired applications and properties.

Polymer nanocomposites are hybrid materials, in which nano-sized particles, often oxides, are highly dispersed in polymer matrices. The advantage of the nanocomposites is at the realization of reinforcement and functionalization at a particle loading much lower than those required for microcomposites. Their properties are largely affected by the morphology and the dispersion level of nanoparticles, and the sol-gel reaction has been a choice for *in-situ* fabrication of dispersed oxide nanoparticles in polymer solution, solvent-swollen polymer, and molten polymer [34–41]. A molecular precursor is uniformly dissolved in or mixed with polymer, and then converted into dispersed oxide nanoparticles, in which macromolecules suppress excessive growth and agglomeration of the formed nanoparticles by physical confinement or chemical hosting. Likewise, macromolecular environments can offer an access to nanosized oxides for the sol-gel reaction even without the presence of a template with well-defined geometry. Recently, we have

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reported *in-situ* fabrication of silica within an amorphous space of semi-crystalline polypropylene (PP): Metal alkoxide was impregnated in a PP film with the aid of supercritical CO<sub>2</sub> (scCO<sub>2</sub>), followed by the sol-gel synthesis of silica [42]. Thus formed silica was nano-sized and uniformly dispersed in the film to afford well-defined PP-based nanocomposites in an *in-situ* manner. It was found that the size of formed silica nanoparticles was comparable to the amorphous thickness (<10 nm), which was much smaller than particles fabricated in a hydrocarbon solvent. Moreover, the mass fractal dimension of the silica nanoparticles determined by small-angle X-ray scattering was close to 2, *i.e.* plate-like rather than 3 for spheres. All these observations suggested that the fabrication of the silica nanoparticles were sterically confined in the amorphous nano-space of PP, and this assumption has motivated us to realize a new template method using the higher-order structure of a semi-crystalline polymer as a template for the sol-gel reaction. It is expected that the morphology of oxide nanoparticles can be controlled through the higher-order structure of a polymer that is easily modified by usual crystallization conditions.

The purposes of the present study are as follows:

- i) To control the morphology of silica nanoparticles through the higher-order structure of PP. The higher-order structure of a PP film, especially the amorphous thickness (later defined in Eq. (3)), was modulated by varying quenching and annealing temperatures. PP films with different higher-order structures were impregnated with silicon alkoxide using scCO<sub>2</sub>, which was subsequently converted into nano-sized silica. The morphology of the formed nanoparticles was characterized and compared with the higher-order structure of PP as a template to reveal the feasibility of the new template method;
- ii) To investigate a relationship between the morphology of synthesized silica and mechanical properties of resultant nanocomposites. It is well known that physical properties of polymer nanocomposites are strongly dependent on the morphology of nanoparticles. However, it has been difficult to individually discuss the impact of the morphology, since the dispersion of nanoparticles also depends on the morphology in conventional melt-mixing. The proposed method provided a series of PP/silica nanocomposites with different nanoparticle morphologies at uniform dispersion, offering an ideal model system for the said issue.

We have successfully proved the feasibility of a new sol-gel template synthesis for nano-sized oxides using the higher-order structure of a semi-crystalline polymer as a template. It was found that the content of formed silica nanoparticles became proportional to the amorphous phase content of PP, and the size and mass fractal dimension of the nanoparticles were controlled by the amorphous thickness of PP. It was also revealed that the size and mass fractal dimension of the formed silica nanoparticles correlated with the storage modulus of the nanocomposites in an exponential manner.

## 2. Experimental

### 2.1. Materials

Isotactic PP pellet with the melt flow rate of 5.0 g/10 min and *mmmm* of 95 mol% was donated by Japan Polypropylene Co., Ltd. Tetra-*n*-propoxysilane (TPOS) was used as a silica precursor.

### 2.2. Sample preparation

PP films with different crystallinities and stacked lamellar

structures were prepared by varying quenching and annealing temperatures. The PP pellet was hot pressed into a 100- $\mu$ m film at 230 °C under 20 MPa for 5 min. The film was quenched at either 100, 120, 130 or 140 °C, followed by the crystallization at the corresponding temperature for 6 h. Otherwise, the film was once quenched at 0 °C for 2 min, and then subjected to annealing at either 100 or 120 °C for 6 h. Thus prepared films were designated as PP-100, PP-120, PP-130, PP-140, PP-0-100, and PP-0-120 according to their thermal history.

A PP film and 4.2 mL of TPOS were charged in a 50 mL high-pressure stainless steel reactor connected to a high-pressure pump. The film was impregnated with TPOS using scCO<sub>2</sub> as a medium at 80 °C and 165 kg/cm<sup>3</sup> for 3 h. After depressurization, the PP film was immediately transferred into a glass vessel that contained an aliquot volume of conc. HCl. The film was treated with HCl vapor for 24 h at 80 °C to fully convert TPOS into silica. The completion of the sol-gel reaction was confirmed by IR (Jasco, FT/IR-4100, Fig. S1) and thermogravimetric analysis.

### 2.3. Characterization

The higher-order structure of a PP film (before the silica synthesis) was characterized. Wide-angle X-ray diffraction (WAXD) was performed on a Rint2000 diffractometer (Rigaku) in a reflection mode with CuK $\alpha$  radiation operated at 40 kV and 30 mA. The diffraction patterns were recorded in a 2 $\theta$  range of 10–30° with a step size of 0.02°. The weight fraction crystallinity ( $X_w$ ) of a sample was evaluated and converted into the volume fraction crystallinity ( $X_{vol}$ ) according to

$$X_{vol} = \frac{\frac{X_w}{\rho_c}}{\frac{X_w}{\rho_c} + \frac{100 - X_w}{\rho_a}} \quad (1)$$

where the densities of the crystalline and amorphous phases ( $\rho_c$  and  $\rho_a$ ) are 0.95 and 0.85 g/cm<sup>3</sup>, respectively. The long period ( $l$ ) of the stacked lamellar structure of a PP film was evaluated by small-angle X-ray scattering (SAXS, Rigaku, Smartlab) using CuK $\alpha$  radiation operated at 40 kV and 30 mA. The measurements were performed in a transmission mode over a 2 $\theta$  range of 0.06–5° with a step size of 0.02°. The obtained SAXS profiles were Lorentz-corrected, and the long period was evaluated from the peak-top position ( $q_{max}$ ) based on the Bragg equation. The lamellar and amorphous thicknesses ( $l_c$  and  $l_a$ ) were then calculated according to

$$l_c = \frac{X_{vol} l}{100} \quad (2)$$

$$l_a = \frac{(100 - X_{vol}) l}{100} \quad (3)$$

respectively. The spherulite structure of a PP film was observed by polarizing optical microscope (POM, Olympus, B201) at room temperature.

The content of silica formed in a PP film was determined by thermogravimetric analysis (TGA, Mettler Toledo, TG50). The temperature was increased up to 600 °C at a heating rate of 10 °C/min under dry air of 50 mL/min, and the silica content was calculated as the weight fraction of inorganic residue at 600 °C. The dispersion and morphology of silica nanoparticles synthesized in a PP film were observed by a transmission electron microscope (TEM, Hitachi, H-7650) at the acceleration voltage of 100 kV. A specimen with the thickness of 100 nm was prepared by an ultramicrotome (Leica ULTRACUT FCS). The morphological characteristics of silica nanoparticles were acquired using SAXS based on the above-mentioned

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