



# Sol–gel synthesis of nano-sized silica in confined amorphous space of polypropylene: Impact of nano-level structures of silica on physical properties of resultant nanocomposites



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## ABSTRACT

Polypropylene (PP)/silica nanocomposites were prepared by the sol–gel reaction of silicon alkoxide that was impregnated in the confined amorphous nanospace of PP with the aid of supercritical carbon dioxide. This novel technique enabled us to prepare nanocomposites having a variety of silica morphology without altering the higher-order structures of PP, being ideal to study relationships between the silica morphology and mechanical properties of the nanocomposites. The synthesized silica particles were highly dispersed in PP with dimensions comparable to the amorphous thickness (<10 nm), while their mass fractal dimension acquired by small-angle X-ray scattering was dependent on the sol–gel conditions. We found that the Young's modulus as well as the storage modulus in melt viscoelastic measurements was negatively correlated with the mass fractal dimension of silica nanoparticles: A lower mass fractal dimension resulted in not only higher reinforcement but also percolation network formation at a lower silica loading.

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## 1. Introduction

Polymer nanocomposites have attracted great attention in these two decades as an attractive way to attain drastic improvements in various properties (such as mechanical strength, gas barrier, heat resistance, etc.) at a small content of nano-sized filler. In comparison with micron-sized filler, the nano-sized filler offers much shorter particle–particle distance and much greater interfacial area with polymer. Thus enlarged filler–filler and polymer–filler interaction in nanocomposites facilitate the formation of network structures at a practical filler content, a key for constructing a pathway of load transfer [1–4] and exploiting the electro- and thermo-conducting properties of filler [5–8].

The term “percolation threshold” is the minimum content of filler which is required to form a network structure. While the increase of the filler content necessarily leads to the network formation, the percolation at a small filler content is practically important in terms of cost, density, and embrittlement all adversely affected by excess loading. The percolation threshold is affected by various factors, for example, the aspect ratio and dispersibility of

filler particles as well as the polymer chemical structure and molecular weight [3,4,9–22]. However, the most fundamental parameter is the nano-level dispersion of filler particles in polymer. In this light, several groups attempted to precisely control the dispersion of filler for establishing relationships between the filler dispersion and physical properties of resultant nanocomposites (structure–property relationship) [23–27].

Akcora et al. successfully controlled the dispersion of spherical filler in amorphous polystyrene by utilizing self-assembly of the filler particles, and concluded that low-dimensional aggregates with the morphology of one-dimensional string or two-dimensional sheet morphology result in much higher reinforcement and lower percolation thresholds, compared with zero-dimensional uniform dispersion and three-dimensional compact aggregates [3]. Jouault et al. also presented a self-assembly-based novel methodology to form small aggregates with fractal-like morphology in polystyrene over a wide range of filler contents [4]. They observed the appearance of a solid-like behavior in melt linear viscoelastic measurements at the silica content as small as 3 vol%, while the percolation threshold was determined as 7 vol%. The template method is an alternative strategy to provide such low-dimensional aggregates in polymer through aggregation of filler particles within confined spaces (templates) [16–22]. Significant reductions in the percolation threshold were reported by localizing

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filler particles at boundaries in co-continuous morphology of immiscible polymer blends with co-continuous morphology [16–18], and by concentrating filler particles in interparticle voids of polymer particulates [19–22]. The template approach has an advantage to shape the dispersion structures of nanoparticles by utilizing predefined spaces, but it has been rarely employed for studying structure–property relationships.

Polypropylene (PP) is one of the most widely used plastics from commodity to specialty applications due to its comprehensive advantages in cost, thermal properties, mechanical and rheological properties, environmental load and so on. Motivated by its huge market, a lot of research has been done on PP-based nanocomposites. Especially, the largest efforts were devoted to alleviate poor dispersion of nanoparticles and weak interfacial connections between PP and nanoparticles. For example, the addition of a compatibilizer such as maleic anhydride-grafted PP is the most adopted approach to improve the dispersion of nanoparticles [28–30]. Grafting polymeric chains onto nanoparticles is a promising approach to remedy both the poor dispersion and weak connection [31–34]. However, these solutions generally promote the homogeneous dispersion (i.e. zero-dimensional) of nanoparticles, and an attempt to manufacture dispersion structures having intermediate fractal dimensions other than three and zero is highly desired, which is essential not only to lower the percolation threshold but also to establish the said structure–property relationships.

The main difficulties are obviously attributed to the poor compatibility of PP with nanoparticles, easily falling into three-dimensional aggregates, and to the poor solubility of PP in polar solvents, making the controlled self-assembly strategy inapplicable. Another serious problem is related to phenomena that occur during the crystallization of polymer in the presence of nano-sized filler: The addition of nano-sized filler generally affects the crystallization behavior of polymer through nucleation effects and/or confined crystallization [35–40]. Therefore, physical properties of nanocomposites are not merely affected by the dispersion structure of filler, but also affected or even dominated by differences in polymer higher-order structures that originate from dependence of the polymer crystallization on the filler dispersion. It is also known that the growth of lamellar structures changes the placement of each nanoparticle nanoparticles and consequently perturbs the dispersion of filler which are once designed in melt [41].

In order to control the dispersion structures of filler and to establish structure–property relationships for PP-based nanocomposites, we sought an approach to introduce filler into predefined higher-order structures as a template without using usual melt- or solution-blending processes. Sun et al. presented a novel route to prepare PP-based nanocomposites, which consists of impregnation of metal alkoxide in a PP film with the aid of supercritical CO<sub>2</sub> (scCO<sub>2</sub>) and subsequent filler formation via sol–gel reaction [42]. Since scCO<sub>2</sub> can disperse metal alkoxide into the swollen amorphous region without dissolving the crystal part, this method is expected to enable individual control of polymer higher-order structures and filler dispersion structures. Furthermore, the sol–gel process in confined spaces such as mesopores is a scientifically attractive way to produce isolated nanoparticles [43–45]. In this light, metal oxide particles synthesized in low-dimensionally confined polymer amorphous nanospaces is an interesting and important target of study.

The purposes of the present study are twofold: i) To control the structure of silica nanoparticles in PP, based on the impregnation of silicon alkoxide with scCO<sub>2</sub> and subsequent sol–gel reaction, and ii) to establish relationships between the structure of the formed nanoparticles and physical properties of the nanocomposites. Silica particles formed in the amorphous region of PP were uniformly

dispersed in the matrix with the sizes becoming less than 10 nm. The mass fractal dimension of the silica nanoparticles varied between two and three according to the kinds of employed silicon alkoxide and catalysts. It was found that the mass fractal dimension of the nanoparticles was well correlated with the Young's modulus in solid state and low-frequency storage modulus in molten state, where a lower dimension led to higher reinforcement.

## 2. Experimental section

### 2.1. Materials

Random PP ( $M_w$ :  $1.6 \times 10^5$ , ethylene content: 2.5 wt%, donated by Japan Polypropylene Co., Ltd.) was selected as a matrix to increase the volumetric ratio of the amorphous region, where silicon alkoxide is impregnated. Tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), tetra-*n*-propoxysilane (TPOS) and tetra-*n*-butoxysilane (TBOS) were used as silica precursors.

### 2.2. Sample preparation

The PP pellet was hot pressed at 230 °C under 20 MPa for 5 min, and then stepwisely quenched at 100 °C for 5 min and at 0 °C for 2 min to obtain a film with the dimension of  $30 \times 40 \times 0.1 \text{ mm}^3$  and the crystallinity of 49 wt%. PP/silica samples were prepared by two steps: (1) impregnation of silicon alkoxide in the PP amorphous region using scCO<sub>2</sub>, and (2) subsequent sol–gel reaction of the precursor in the matrix. In detail, a specified amount of liquid silicon alkoxide (1.5–30 mmol) was introduced in the bottom of a 50 ml stainless steel reactor, on which a PP film was placed. After sealing the reactor, CO<sub>2</sub> gas was forcibly introduced to produce a supercritical state at 80 °C under 165 kg/cm<sup>3</sup>. ScCO<sub>2</sub> not only completely dissolves silicon alkoxide but also swells the amorphous region of PP. The impregnation of silicon alkoxide was continued for 12–36 h with the aid of scCO<sub>2</sub>. After that, the film containing silicon alkoxide was immediately transferred in a glass reactor, where the sol–gel reaction was performed for 0.5–24 h in the presence of either HCl vapor at 80 °C or NH<sub>3</sub> vapor at 60 °C. The film was hung in the glass reactor, while an aliquot volume of conc. HCl(aq) or conc. NH<sub>3</sub>(aq) was placed on the bottom of the glass reactor, thus preventing the direct contact between the film and liquid. It should be noted that when the film was soaked in acidic or alkaline aqueous solution, silicon alkoxide was completely transferred to the liquid phase and did not remain in the film.

### 2.3. Characterization

Fourier transform-infrared spectroscopy (FT-IR, JASCO FT/IR-6100) was employed to detect the formation of silica in PP film. The silica content in PP/silica was determined by thermogravimetric analysis (TGA, Mettler Toledo, TG50), where the inorganic residue was weighted after incinerating organic components at 600 °C under air.

Sample crystallinities were measured by wide-angle X-ray diffraction (WAXD, Rigaku, Rint2000). The measurements were performed in a reflection mode at room temperature with CuK $\alpha$  radiation operating at 40 kV and 30 mA with the step of 0.02 from 10° to 30°.

The dispersion and particle morphology of silica synthesized in PP were observed by a transmission electron microscope (TEM, Hitachi, H-7650). TEM specimens with the thickness of 100 nm were prepared by an ultramicrotome with a Leica ULTRACUT FCS. The morphology of silica that was prepared in aliphatic hydrocarbon solvent (tetradecane) was observed by a scanning electron microscope (SEM, Hitachi, S-4100) at an accelerating voltage of

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