



Versatile strategy for fabrication of polypropylene nanocomposites with inorganic network structures based on catalyzed *in-situ* sol–gel reaction during melt mixing



Kei Kaneko, Nitin Yadav, Kengo Takeuchi, Bulbul Maira, Minoru Terano, Toshiaki Taniike*

School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

ARTICLE INFO

Article history:

Received 16 April 2014

Received in revised form 17 July 2014

Accepted 21 July 2014

Available online 4 August 2014

Keywords:

A. Nano composites

A. Polymer–matrix composites (PMCs)

A. Oxides

A. Nano particles

E. Sol–gel methods

ABSTRACT

A versatile strategy based on a catalyzed *in-situ* sol–gel reaction in melt mixing is presented for the fabrication of polypropylene (PP) nanocomposites that equip inorganic network structures. PP nanocomposites with TiO₂ network structures were obtained by melt mixing PP powder which was preliminarily impregnated with titanium alkoxide and a catalytic component. The addition of catalytic components, especially hindered amine stabilizer, was found to be effective not only for the acceleration of the *in-situ* sol–gel reaction but also for improved dispersion of formed inorganic nanoparticles. The obtained PP/TiO₂ nanocomposites exhibited the disappearance of the terminal flow at ca. 3 wt% of the TiO₂ content, indicative of the network formation. Moreover, the PP/TiO₂ nanocomposite films exhibited distinct optical properties: Not only high transparency for visible lights due to the excellent dispersion of the made nanoparticles but also absorption of UV lights, where absorption edges are tunable through a quantum effect for nanosized particles.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Polymer nanocomposites have attracted considerable attention as they offer a multitude of outstanding properties such as high strength and stiffness [1–3], flame retardancy [4], chemical resistance [5], electrical conductivity [6], high refractive index [7], superhydrophobicity [8], and gas barrier properties [9]. These hybrid composites offer synergetic combination of unique properties of original polymer and nanomaterials. A pioneering work by Toyota researchers discovered the immense potential of polymer nanocomposites and generated a great enthusiasm among material scientists [10]. They reported that as little as 2 vol% of exfoliated montmorillonite doubled the tensile modulus of Nylon-6 without sacrificing its impact resistance. The heat distortion temperature of the nanocomposite was 87 °C higher than that of Nylon-6, exploring applications under high-temperature environments like under-the-hood parts in automobiles. Moreover, high-performance but economical plastics that equip both easy processability of polymer and novel functionalities of inorganic materials such as electrical, dielectric and thermal properties can be fabricated by introducing three dimensional network structures of inorganic

fillers within polymer matrices. The significance of inorganic networks for the origin of potentially novel functionalities in polymer has been well documented in literature [6,11–14]. Park et al. found that a network of single-walled carbon nanotube (SWNT) in polyimide enhanced the electrical conductivity by orders of magnitudes at a nanotube loading of only 0.1 vol% [6]. Du et al. reported that the addition of SWNT in a poly(methyl methacrylate) (PMMA) matrix brought about great improvements in the thermal stability and the flame retardancy, where a networks of SWNT significantly reduced the heat release rate of PMMA [11]. Sun et al. synthesized nanosized SiO₂ networks distributed uniformly in a polypropylene (PP) matrix and thereby obtained significant increase in the mechanical properties [12]. Cassagnau et al. studied the morphology and viscoelasticity of PP/TiO₂ nanocomposites [13]. They found that a solid-like behavior in the terminal relaxation appeared as a result of the formation of an aggregate network. Tong et al. reported that polyimide/TiO₂ nanocomposites that equip TiO₂ networks were superior to the original polyimide in terms of thermal stability, optical transparency, mechanical properties and dielectric constants [14].

So far, nanocomposites have been studied for many kinds of polymer such as Nylon, PP, polyethylene, polystyrene, poly(ethylene oxide) and polyimide, PMMA, and so on. Among these, PP nanocomposites are of special interests due to their outstanding

* Corresponding author. Tel.: +81 761 51 1630; fax: +81 761 51 1635.

E-mail address: taniike@jaist.ac.jp (T. Taniike).

industrial importance. PP has wide applications in a variety of fields due to its excellent characteristics such as widely adjustable mechanical properties, low production cost, high melting temperature, excellent processability, high resistance to water and chemical environments, high reusability/recyclability being free from hazardous constituents, and so on. Due to economic and environmental concerns, further expansion of the application area of PP is highly desired, in which compounding of PP with nanomaterials has been long expected as one of the key techniques. Nevertheless, the present situation for the development and application of PP nanocomposites is far below the expectation. The main difficulty arises from poor compatibility of PP with inorganic fillers: Nano-level dispersion of fillers in PP is challenging due to the absence of polar groups. It is also notable that most of nanofillers greatly accelerate the oxidative degradation of PP [15,16]. The most widely employed remedies for the dispersion problem are the addition of a compatibilizer such as maleic anhydride grafted PP (MAPP) and organic modification of filler surfaces [17,18]. However, MAPP forms a soft interfacial layer between the matrix and fillers to restrict mechanical improvements [19–21] and also accelerates the oxidative degradation [22,23]. Alternative approaches without the usage of a compatibilizer have been proposed such as grafting polymer chains to filler surfaces [24–26] and *in-situ* polymerization in the presence of fillers that support catalytic components [2]. Especially, the former approach endows not only nano-level dispersion of fillers but also interfacial reinforcement through entanglement, inter-diffusion, and/or physical crosslinking [27,28]. However, these approaches are not specialized for introducing inorganic networks in PP, where the random nature of the dispersion necessitates the addition of nanofillers over a relatively high percolation threshold for the network formation.

The sol–gel technique is regarded as one of the most successful methods for controlled synthesis of network structures of inorganic fillers within polymer matrices [12,13,29]. It allows the incorporation of metal oxide networks into polymer matrices as a result of hydrolysis and condensation reactions of metal alkoxide. In typical preparation, the sol–gel reaction of metal alkoxide is performed in solution or melt of polymer, where homogeneous dissolution of metal alkoxide in the medium is a prerequisite for nano-level dispersion of the resultant metal oxides [13,29]. In the case of PP, neither the solution nor the melt blending approaches are applicable, since most of solvent cannot dissolve PP at mild temperature and typical metal alkoxide is not miscible with molten PP. Sun et al. [12] reported a novel two-step method for the fabrication of nanosized SiO₂ networks uniformly distributed in PP: (i) impregnation of tetraethoxysilane in a PP thin film with the aid of supercritical CO₂ as a carrier and swelling agent, and (ii) subsequent sol–gel reaction under aqueous HCl for 3 days. Possible limitations of this method are the necessity of thin films (since both of the steps contain the permeation of molecules in solid PP) and the inapplicability to large-scale production based on conventional melt mixing technology. Another two-step approach recently presented by Bahloul et al. [13] consisted of (i) melt mixing of titanium *n*-butoxide with PP in a co-rotating twin screw extruder, and (ii) completion of the sol–gel reaction in hot water for 3 days. Though they successfully observed the formation of a percolation network composed by TiO₂ primary particles smaller than 5 nm, it still required quite a long time to complete the sol–gel reaction albeit the high reactivity of titanium alkoxide.

The objective of the present study is to develop a more versatile strategy for the large-scale fabrication of nanosized metal oxide networks in a PP matrix within a short period of time, based on melt mixing technology. We report that PP powder preliminary impregnated with titanium alkoxide and a catalytic component can give such a solution: Melt mixing of the wet PP powder resulted in the formation of TiO₂ networks with extremely nice

dispersion without any post reactions. Moreover, nanocomposite films achieved UV absorption properties whose absorption edges were determined by a quantum effect for nanosized materials without losing the visible transparency.

2. Experimental

2.1. Materials

PP powder ($M_w = 2.6 \times 10^5$, $M_w/M_n = 5.69$ and $mmmm = 98$ mol%) was synthesized by slurry polymerization of propylene with a MgCl₂-supported Ziegler–Natta catalyst. Titanium *n*-butoxide (Ti(OnBu)₄), titanium isopropoxide (Ti(OiPr)₄) and titanium ethoxide (Ti(OEt)₄) were used as an inorganic precursor for the sol–gel reaction, while TiO₂ nanoparticles (NT-500B, Tayca Corporation diameter = 35 nm) were used to prepare a reference nanocomposite. Bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate (LA-77, donated by ADEKA Corporation), citric acid (CA) and MAPP were used as a catalyst. Octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (AO-50, donated by ADEKA Corporation) was used as a stabilizer.

2.2. Sample preparation

Four procedures were tested for the fabrication of PP/TiO₂ nanocomposites, whose details are given below.

Procedure 1 for Sample A: 50 g of the PP powder was directly melt mixed with Ti(OnBu)₄ (whose amount was decided to satisfy 5.0 wt% of TiO₂ at the full conversion) in the presence of 1.0 wt% of AO-50 using an internal mixer (Labo Plastomill, Toyo Seiki Seisakusho Ltd.) at 180 °C and 100 rpm for 15 min.

Procedure 2 for Samples B–D: 50 g of the PP powder was dry impregnated with Ti(OnBu)₄ (whose amount corresponded to 3.0 wt% of TiO₂) containing 1.0 wt% of AO-50 in a three-necked flask stirred at 150 rpm and 100 °C for 6 h. Ti(OiPr)₄ or Ti(OEt)₄ was also employed instead of Ti(OnBu)₄. The resultant wet powder was subsequently melt mixed using the conditions mentioned in Procedure 1.

Procedure 3 for Samples E–I: Procedure 3 is almost the same with Procedure 2, except the addition of 0.5 wt% of a catalytic component (LA-77 and CA) or 5.0 wt% of MAPP in the dry impregnation.

Procedure 4 for Sample NP: A reference sample was prepared by melt mixing 50 g of the PP powder with 5.0 wt% of TiO₂ nanoparticles in the presence of 1.0 wt% of AO-50 using the conditions mentioned in Procedure 1.

After the melt mixing, each sample was hot pressed at 230 °C and 20 MPa for 10 min, followed by quenching at 100 °C for 5 min and subsequently at 0 °C for 5 min. The obtained sample films with the thickness of 100 μm were used for various analyses except IR measurements, where the thickness was reduced to 30 μm.

2.3. Sample analyses

The progress of the sol–gel reaction and the formation of TiO₂ were qualitatively confirmed by FTIR (JASCO FT/IR-6100). Transmission spectra were acquired using 30 μm-thick sample films at a resolution of 4 cm⁻¹ with 24 scans. Thermogravimetric analysis (TG, Mettler TG-50) was used to determine the amount of fabricated TiO₂ in the PP/TiO₂ nanocomposites. Samples were heated up to 600 °C at 20 °C/min and the remaining amount was regarded as that of TiO₂. The dispersion of TiO₂ nanoparticles in the matrix was observed by transmission electron microscope (TEM, Hitachi H-7100). TEM specimens with the thickness of 100 nm were

Download English Version:

<https://daneshyari.com/en/article/820187>

Download Persian Version:

<https://daneshyari.com/article/820187>

[Daneshyari.com](https://daneshyari.com)