



Thermal-oxidative effect of a co-condensed nanosilica-based antioxidant in polypropylene



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ABSTRACT

Antioxidant in form of hindered phenol structure is commonly used to prolong the service life of polymer, while the low molecule antioxidant has defect for its low thermal stability and physical loss. Herein, the feasibility of using co-condensed silica immobilized antioxidant (denoted as SN-NH₂-AO) to improve the thermal-oxidative stability of polypropylene (PP) was evaluated. Firstly, SN-NH₂-AO was prepared by immobilization of 3,5-di-*tert*-butyl-4-hydroxyphenylpropionic acid (AO) on the surface of co-condensed silica (SN-NH₂) which was synthesized by co-hydrolysis and condensation of tetraethoxysilane and aminopropyltriethoxysilane. Compared with AO, SN-NH₂-AO exhibited higher thermal stability. Further, SN-NH₂-AO was incorporated into PP by melt blending. The incorporation of SN-NH₂-AO could not only disperse well in PP matrix but also improve the thermal-oxidative stability of PP distinctly. It was found that although the anti-oxidative efficiency of SN-NH₂-AO was slightly inferior to AO, SN-NH₂-AO exhibited superiority on anti-extraction property.

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1. Introduction

Degradation caused by circumstance (temperature, UV-light, humidity, etc.) is an inevitable phenomenon for polymeric materials during their processing, usage and storage periods, which leads to the deterioration of the performances. Therefore, the anti-aging of polymers is always an attractive topic in both the industry fields and the fundamental research [1,2]. Additives, such as antioxidants and light stabilizers, are used to minimize the degradation of polymers [3–6]. However, additives are restricted by physical loss, such as volatilization, migration and extraction during their service because of the low molecular weight and low thermal stability. To overcome these shortages, new additives are developed mainly by the following three methods: (1) increasing the molecular weight [7,8], (2) grafting onto the polymer backbone [6,9], and (3) immobilizing onto the surface of nanoparticles [10–14].

In the last decade, there is a growing interest in immobilizing the low molecule additives onto the surface of nanoparticles. In 2007, Gao et al. firstly synthesized a nanosilica-immobilized-antioxidant by using a bi-functional amino-silane compound as a *bridge* [10,11]. They found that the antioxidant-immobilized-nanosilica could prevent thermal aging significantly and retain favorable stability in the matrix of polyolefin against extraction. After that, by using various kinds of silane as a *bridge*, varied silica-immobilized low molecule additives were successively reported. Huang [15,16] and Pan et al. [17] synthesized an aminodiphenylamine immobilized silica via (3-glycidyloxypropyl)-trimethoxysilane which could improve the mechanical property and thermal stability of rubbers. Jia et al. [18,19] reported an environmentally friendly rubber antioxidant (silica-supported 2-mercaptobenzimidazole) with lower color contamination and volatility. Besides of antioxidant, UV stabilizer was also grafted onto silica, exhibiting excellent retardation to degradation of polyolefin under UV exposure [20]. Deligiannakis et al. [21] investigated the anti-oxidant mechanism of a nano-antioxidant material (Gallic acid grafted silica nanoparticles, Silica-GA). They found that Silica-GA still could scavenge radicals by H-atom transfer mechanism, indicating that immobilization did not change the anti-oxidant

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mechanism of GA.

As mentioned above, the post-modification method, *videlicet*, grafting organosilane on the surface of silica nanoparticles, was commonly used to prepare the functionalized silica with anti-aging effect for polymers. However, due to the nonuniform dispersion of the functionalization and the heavy use of toxic organic solvent, the modification method was restricted in application [22,23]. What is worse, the grafting degree was usually low, leading to the poor loading of functional groups [24,25]. The *in situ* modification method, called co-condensation method, was proposed by Parish et al. [26]. In 1999, Hüsing et al. found that when a organosilane contained a strongly basic substituent (such as amino group), the reaction can undergo a self-catalyst process without adding other catalyst like ammonia [27]. After that, the co-condensation method has attracted increasing attention when producing modified silica [28,29]. Compared with post-modification method, a major superiority of co-condensation method, except the reduction of organic solution dosage, was the content of organic group can be tuned by the initial ratio of reagent [25,27,29–32].

In comparison to the low grafting degree of the post-modification, the co-condensation method was more appropriate to prepare the functionalized silica. Hence, we focused on the preparation of AO-modified silica, which was obtained by co-condensed method. Particularly, amino-functionalized silica (SN-NH₂) was synthesized by co-condensation between TEOS and APTES, and then reacted with a reactive antioxidant (AO-Cl) on its surface to prepare the co-condensed silica immobilized antioxidant (SN-NH₂-AO). The thermal-oxidative stability and anti-oxidative efficiency of PP/SN-NH₂-AO nanocomposite was evaluated in comparison with PP/AO composite. The anti-extraction properties of SN-NH₂-AO in PP were assessed too.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS) was purchased from Xilong Chemical Co., Ltd. Aminopropyltriethoxysilane (APTES) and 3,5-di-*tert*-butyl-4-hydroxyphenyl-propionic acid (AO-COOH) were bought from Alfa Aesar and used as-received. The unstabilized polypropylene, with melt flow index (MFI) is 5.7–7.0 g/10 min, was supplied by Liaoh Petrochemical Company. The absolute ethanol and toluene were all of analytical grade and produced by Beijing Chemical Works. All materials were used as-received without further treatment.

2.2. Synthesis of functionalized silica nanoparticles

2.2.1. Preparation of co-condensed nanosilica SN-NH₂

The co-condensed nanosilica was prepared by modified Rahman method [29]. A quantity of TEOS and APTES (total Si concentration was 0.9 mol/L) with the ratio of 1:4 (mol: mol) were added into 225 mL ethanol and stirred magnetically for 10 min. Then 8 mL H₂O were added into the system and further reacted for 3 h to obtain an opaque admixture. The product was filtered and then washed 3 times with ethanol. Subsequently, the filter cake was dried at 120 °C in a vacuum oven overnight under.

2.2.2. Preparation of co-condensed silica immobilized antioxidant

The preparation of the co-condensed silica immobilized antioxidant was conducted through acylating chlorination of AO and succeeding acylation of the nanosilica. Typically, 6 g AO-COOH was dissolved in toluene and then 5 g thionyl chloride were added under nitrogen atmosphere. The mixture reacted under refluxing until no hydrochloric acid was generated. The unreacted thionyl

chloride and toluene were removed through vacuum distillation. The acyl chloride product, 3,5-Di-*tert*-butyl-4-hydroxyphenyl-propionic chloride, was collected and denoted as AO-Cl. Then the AO-Cl was dissolved in anhydrous toluene and added dropwise into the SN-NH₂ suspension in toluene. The reaction mixture was stirred for 24 h at room temperature under nitrogen atmosphere. Finally, the product was filtered and then washed 3 times with ethanol. After dried at 120 °C in a vacuum oven overnight, the co-condensed silica immobilized antioxidant, abbreviated as SN-NH₂-AO, was obtained. The synthesis route was illustrated in Scheme 1.

2.3. Preparation of PP composites

The PP composites were prepared by melt blending using an HAAKE PolyLab OS RheoDrive 7 (ThermoFisher Scientific, Germany) at 180 °C with a low rotor speed of 20 rpm for the first 2 min for preheating, then with a high rotor speed of 50 rpm for another 5 min for complete mixing. Prior to the melt blending, the SN-NH₂ and SN-NH₂-AO were dried in a vacuum oven overnight at 120 °C. The formulations of the composites were listed in Table 1. Testing specimens were prepared through compression molding at 190 °C. Films with thickness of 40 μm were used for accelerated aging test, while disks with thickness of 500 μm for DSC test and extraction.

2.4. Characterization

Fourier transform infrared spectroscopy (FT-IR) analysis for nanoparticles was carried out using a Perkin-Elmer System 2000 infrared spectrum analyzer in the wave number range of 4000–650 cm⁻¹ with KBr pellets.

X-ray photoelectron spectroscopy (XPS) data was obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al K α radiation. The base pressure is about 3 × 10⁻⁹ mbar. The binding energies are referenced to the C1s line at 284.6 eV from adventitious carbon.

Nuclear magnetic resonance (NMR) spectra were measured using a Bruker Avance III 400 NMR. ²⁹Si MAS NMR (Magic Angle Spinning NMR) measurement was conducted at 53 MHz with a spinning speed of 8 KHz, pulse length and delay of 4 μs and 10 s, respectively. The ¹³C CPMAS-TOSS (Cross Polarization/Magic Angle Spinning– total suppression side band) experiment was operated at 100.38 MHz, with pulse length and delay were of 3 ms and 2 s.

Transmission electron microscope (TEM) image was obtained using a JEOL (Japan) JEM-2200FS instrument with an accelerate voltage of 150 kV. Specimen of TEM was prepared by dropping the dilute silica dispersion on the copper grid covered by carbon-coated film.

Water contact angle (CA) with 3.5 μL deionized water droplet was measured by using a DSA-100 Contact Angle Meter (Germany). The specimen of CA test was prepared by the spin coating technique at 2000 rpm for 10 s [32].

Thermogravimetric analysis (TGA) was carried out using Perkin-Elmer Pyris 1 and TGA 7 thermogravimetric analyzer in nitrogen and air atmosphere respectively. The thermal behavior was characterized by temperature programming from 50 °C to 700 °C at a heating rate of 20 °C/min.

Isothermal thermogravimetric analysis was carried out using a Perkin-Elmer TGA-7 thermogravimetric analyzer at 200 °C in air atmosphere with a flow of 40 mL/min.

Scanning electron microscope (SEM) image was taken on a JEOL S-4300F field emission scanning electron microscope at 5 kV. The specimen of SEM was fractured in liquid nitrogen. The fractured surfaces were coated with Pt to enhance the conductivity before the SEM observation.

The oxidation induction time (OIT) measurement was

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