



Preparation of nanosilica-immobilized antioxidant and the antioxidative behavior in low density polyethylene



Peng Liu, Hanying Tang, Ming Lu, Chong Gao, Feng Wang, Yanfen Ding, Shimin Zhang, Mingshu Yang*

Beijing National Laboratory for Molecular Science, CAS Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

ARTICLE INFO

Article history:

Received 21 March 2016
Received in revised form
17 October 2016
Accepted 21 October 2016
Available online 21 October 2016

Keywords:

Silica
Antioxidant
Low density polyethylene
Thermal oxidative stability

ABSTRACT

This article reports a study of the preparation of nanosilica-immobilized antioxidant (SiO₂-APTMS-AO) and the thermal oxidative stability of low density polyethylene (LDPE) nanocomposites containing SiO₂-APTMS-AO. SiO₂-APTMS-AO was prepared based on the fumed nanosilica which was firstly modified with an aminosilane coupling agent and then reacted with 3,5-Di-*tert*-butyl-4-hydroxybenzoic acyl chloride. Infrared spectroscopy, X-ray photoelectron spectroscopy and thermogravimetric analysis measurements confirmed that the antioxidant group was chemically immobilized onto nanosilica. LDPE/silica nanocomposites were prepared by melt mixing and then pressed into different films. The thermal oxidative stability of the nanocomposites was evaluated by thermogravimetric analysis in air atmosphere, oxidation induction time (OIT) and long-term accelerated thermal aging. The results showed that the SiO₂-APTMS-AO can significant improve the thermal oxidative stability of LDPE nanocomposite. Because SiO₂-APTMS-AO is based on inorganic nano-filler, in comparison to organic antioxidants, it might have advantages in thermal stability and migration stability during processing and application.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Low density polyethylene (LDPE) is mainly used in pipe industry, agricultural film, cable cover, commodity, packaging materials and other fields because of its advantage of easy manufacture, low thermal conductivity and good chemical resistance. Pure LDPE is regarded as a stable polymer and only slowly degradable in contrast to other polymers [1]. Because of the presence of impurities, hydroperoxides and carbonyl groups introduced during high-temperature manufacturing processing, LDPE becomes easy to be degraded under the influence of heat or UV-light [2,3]. Additives are usually added to prevent the degradation of LDPE, such as antioxidant, light stabilizers, antistatic agents et al. [4]. Hindered phenolic antioxidants are recognized as the most important long term heat stabilizer and widely used in LDPE. Because of the low molecular weight, low molecular weight antioxidants are easy to degrade or volatilize during polymer processing or likely to migration and extraction during their long-term usage [5–8]. In

recent years, Viebke, Gedde and coworkers have published a lot of research focused on this topic [9–13]. In order to overcome these drawbacks, several approaches that have been developed. One method is to increase the molecular weight of antioxidants. However, it was found that the high molecular weight of antioxidants, e.g. Irganox® 1010 or Irganox® 1076, also suffered from physical loss under aggressive service conditions [7,8,14]. Another approach is grafting the antioxidant groups onto the polymer backbone [15,16] or copolymerization of monomers with antioxidant-functionalized monomers [17]. Hindered phenol groups were utilized melt free-radical grafting to polyolefin. Recently, several new polymeric antioxidants were achieved by polymerization of monomer-bound via radical polymerization or via ring-opening metathesis polymerization (ROMP) [18–20].

In the recent years, modification of polymers by various nanoparticles have received considerable attention in both academia and industry due to their unique physical and/or chemical properties. In order to increase the thermal and thermo-oxidative stability, LDPE modified with various nanoparticles, e.g. layered double hydroxides [21–23], copper nanoparticles [24], silica [25,26], calcium carbonate [27], single wall or multiwall carbon nanotubes [22,28], layered silicates (clays) [29,30], POSS [31] etc. It

* Corresponding author.

E-mail address: yms@iccas.ac.cn (M. Yang).

was found that attach antioxidants onto the nanoparticles can dramatically improve the extraction resistance and achieve high stabilizing activity.

3,5-Di-*tert*-butyl-4-hydroxybenzoic acid is not a high efficiency antioxidant and often used as an intermediate to prepare other kinds of antioxidant and light stabilizer. In the present work, the immobilized antioxidant (SiO₂-APTMS-AO) was prepared by grafting 3,5-di-*tert*-butyl-4-hydroxybenzoic acid onto silica nanoparticle which acted as solid support. The chemical reaction and structure of SiO₂-APTMS-AO was investigated. The SiO₂-APTMS-AO was then incorporated into LDPE by melt processing. The antioxidative efficiency was evaluated by short-term oxidation induction time and long-term accelerated thermal aging. The experimental results have demonstrated that the SiO₂-APTMS-AO can effectively increase the thermal and thermo-oxidative stability of LDPE.

2. Experimental

2.1. Material

The low density polyethylene without stabilizer (LDPE 112A with a melt flow index of 2.0 g/10 min at 190 °C) was supplied by Yanshan Petrochemical Co LTD, Beijing, China. Aerosil-200 fumed nanosilica (SiO₂, surface area 200 ± 25 m²/g, primary particle size 12 nm, purity 98%) was obtained from Evonik Degussa, and dried in a vacuum oven overnight at 120 °C before use. Thionyl chloride, 3,5-di-*tert*-butyl-4-hydroxybenzoic acid and aminosilane coupling agent 3-aminopropyltrimethoxysilane (APTMS) were purchased from Alfa Aesar and used as-received. The toluene and pyridine were of analytical grade and used after distillation. All other solvents and reagents were used as-received.

2.2. Preparation of functionalized nanosilica

The aminosilane coupling agents modified nanosilica, SiO₂-APTMS, was synthesized as illustrated in Scheme 1. The experimental details have been described in our previous work. The SiO₂-APTMS was dried in a vacuum oven overnight at 120 °C.

3,5-Di-*tert*-butyl-4-hydroxybenzoic acid (AO, 5.0 g) was dissolved in thionyl chloride (20 mL) and the reaction mixture was allowed to reflux until no hydrochloric acid was generated. Then removed the unreacted thionyl chloride by evaporated under reduced pressure. The obtained product was added to the suspension of SiO₂-APTMS (5.0 g) in anhydrous toluene (200 mL) under stirring. Anhydrous pyridine (1.0 mL) was next added drop wise and the mixture was stirred for 24 h at room temperature under nitrogen atmosphere. The obtained product was filtered and washed with anhydrous toluene (200 mL, 3 times) and absolute ethanol (200 mL, 3 times). The nanosilica-immobilized antioxidant

(SiO₂-APTMS-AO) was dried in a vacuum oven overnight at 120 °C.

2.3. Preparation of LDPE/silica nanocomposites

The LDPE/silica nanocomposites were prepared by melt blending using an HAAKE PolyLab OS RheoDrive 7 (Thermo Fisher 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 fumed nanosilica and functionalized nanosilica were dried in a vacuum oven overnight at 120 °C. Several LDPE compounds were prepared and their compositions are listed in Table 1. In LDPE/AO composite, the AO content is 0.31 wt%, equivalent to the molar fraction of the antioxidant in LDPE/SiO₂-APTMS-AO nanocomposite. The prepared materials were pressed into films at 180 °C with an average thickness of 260 μm for TGA and DSC measurements and 40 μm for accelerated aging test.

2.4. Accelerated aging test

The obtained LDPE films (40 μm) were placed in an air oven at 90 °C for thermal aging. At appropriate time intervals, the samples were taken out from the oven and the changes due to thermal oxidative degradation were monitored by Infrared spectroscopy (IR) tests. A Perkin–Elmer System 2000 infrared spectrometer was used to measure the structural changes of LDPE films. Carbonyl index (CI), as determined from IR spectra was used to characterize the extent of degradation of LDPE molecular. It was calculated by Eq. (1)

$$\text{Carbonyl index} = A_C/A_R \quad (1)$$

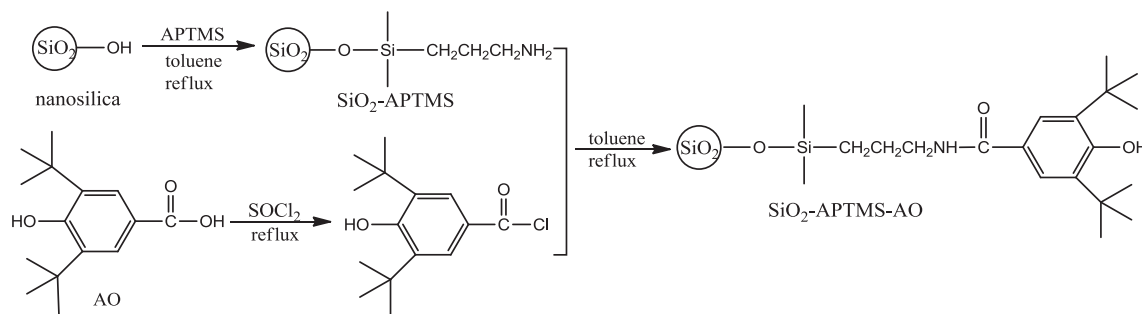
where A_C is the area of the carbonyl absorption band around 1723 cm⁻¹ and A_R is the area of the reference band around 1463 cm⁻¹ [32].

2.5. Characterizations

IR analysis was carried out using a Perkin–Elmer System 2000 infrared spectrum analyzer in the wave number range of

Table 1
LDPE and LDPE/silica nanocomposites and their compositions.

Sample	Type of additives	Content of additives (wt%)
LDPE	–	–
LDPE/SiO ₂	SiO ₂	3.0
LDPE/SiO ₂ -APTMS	SiO ₂ -APTMS	3.0
LDPE/AO	AO	0.31
LDPE/SiO ₂ -APTMS-AO	SiO ₂ -APTMS-AO	3.0



Scheme 1. Synthesis of functionalized nanosilica (SiO₂-APTMS-AO).

Download English Version:

<https://daneshyari.com/en/article/5201019>

Download Persian Version:

<https://daneshyari.com/article/5201019>

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